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PLASTICS, THEORY AND PRACTICE
The Technology of High Polymers

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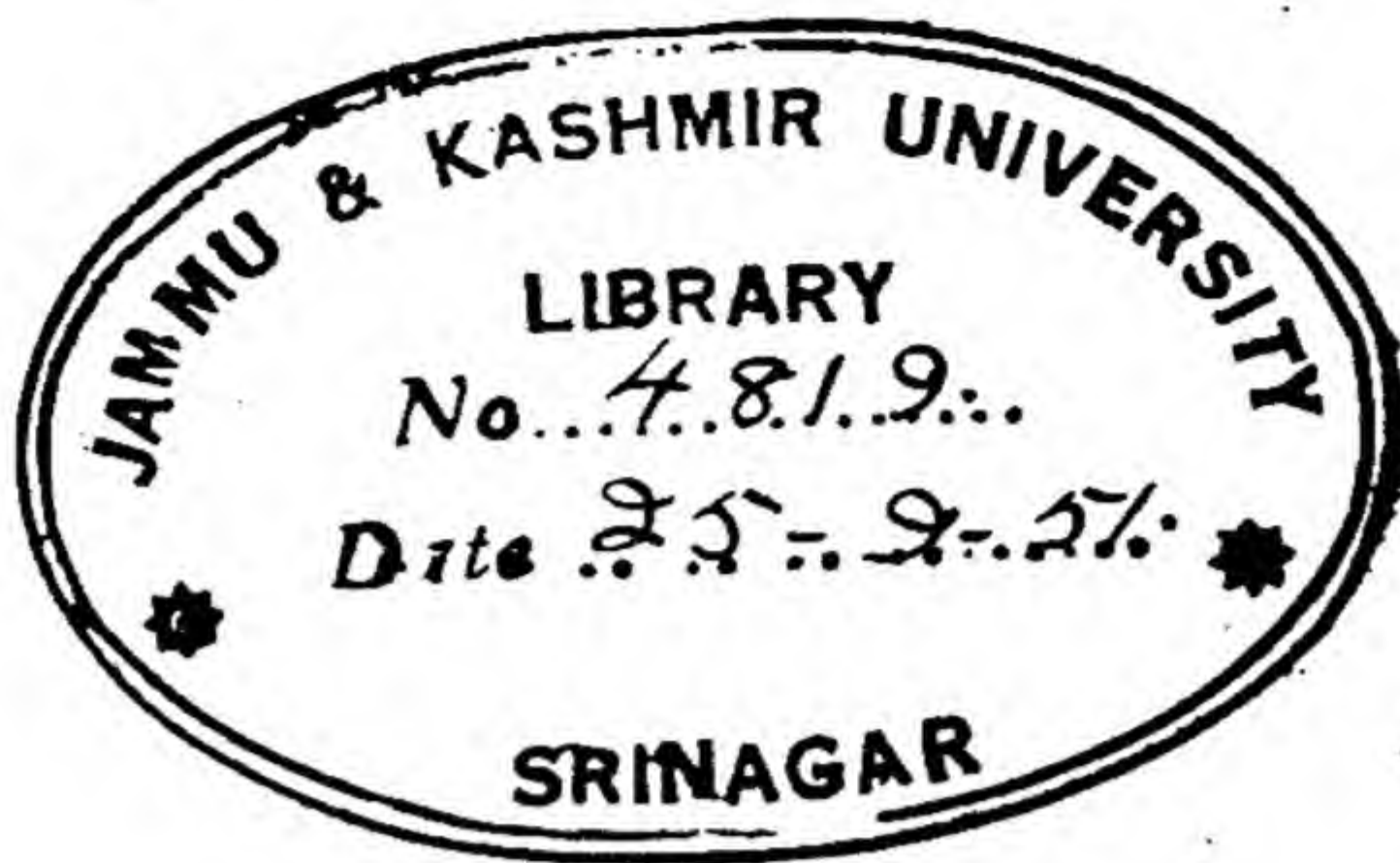
Plastics

THEORY AND PRACTICE

THE TECHNOLOGY OF HIGH POLYMERS

BY

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PREFACE

This book has been prepared with a specific objective in mind—that of "up-grading" the chemist and chemical engineer in the broad field of high polymers. No attempt has been made to teach the reader organic chemistry. It has been assumed that he has reached that stage in his career where he is willing and able to refer to standard texts and handbooks for specific information, much as he would refer to a dictionary for spelling and pronunciation.

The coverage of the field of high polymers is broad, so much so that the expert in any one field of plastics will perhaps not find enough detailed information on his particular field in this text. He will, however, find that the fundamental factors relating to any specific resin or plastic are presented—facts that may be second nature to the expert but not to the worker just becoming familiar with the field of high polymers. To accomplish this broad presentation of the background of high polymers, many liberties have been taken with precise definitions. Viscose and rubber have been presented as resins, a presentation that obviously could be challenged by the expert; yet a majority of the reviewers have been in wholehearted agreement that anyone desiring a background in this field should have a knowledge of the technology of all high polymers, and the generalized definition has much to be said for it in simplifying the approach to the subject.

Methods of fabrication and application are given early in the text, before the reader becomes familiar with the properties of the various classes of resins. The authors believe that the chemist and chemical engineer will grasp the chemistry and chemical structure of each resin quickly, but they may need information regarding methods of fabrication before they are able to relate specific properties with uses. A direct comparison may be made in the field of metallography, where the student is introduced to casting, machining, welding, etc., before he becomes acquainted with the chemistry and physical structure of metals. It is believed that the student of chemistry and chemical engineering will be able to grasp the various factors involved in the fabrication of plastics once he understands the character and properties of high polymers as presented in Part I.

The possible combinations of monomeric materials in the synthesis of new copolymers is so enormous that only those which are now produced commercially or show promise of commercial application are included in this text. In other words, laboratory curiosities are purposely omitted.

Following the discussion of specific polymers, a brief summary is pre-

v

sented giving properties and uses of the materials, usually as molding compositions. Lack of consistency in certain cases is admitted, since it is not always possible to compare types with such a diversity of properties as are found in the commercial plastics and high polymeric materials. However, it is hoped that the tables will be found useful in enabling the reader to remember the principal characteristics of each product.

Trade names of products have purposely been omitted from the body of the text, because it is felt that the polymeric materials should be recognized by their chemical type rather than as products of commercial exploitation. For those who wish to identify trade names, reference can be made to the tables in the Appendix.

The authors wish to acknowledge the valuable help of R. A. Barkhuff, Jr., C. K. Bump, E. F. Fiedler, R. F. Hayes, C. J. Malm, W. I. Patnode, C. H. Penning, J. J. Pyle, E. G. Rochow, and W. L. Semon, in reviewing and criticizing parts or all of this book.

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CHARLES C. WINDING.
R. LEONARD HASCHE.

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ITHACA, N. Y.,
KINGSPORT, TENN.,
    February, 1947.

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INTRODUCTION

Precise definition of a plastic is practically impossible. Either the definition must be incomplete, or it turns out to be more of a general discussion of the possible exceptions and borderline cases than a concise and clear statement of the materials being considered. The simplest definition merely states that a plastic is a material that can be formed by the application of heat and pressure or by pressure alone. Since this statement obviously includes the metals; it can be readily modified by limiting plastic materials to organic compounds. It is at this point that all definitions begin to fall down, as there are many nonmetallic plastics that are not carbon compounds, and there are some that are a mixture of carbon compounds and inorganic elements. For these reasons it is better not to try to be all-inclusive, but to consider a plastic a material that is usually a high molecular weight organic compound that can be, or has been, formed into a definite shape by the application of heat and pressure or pressure alone and that once formed retains its shape under normal conditions. The finished product is so familiar to everyone that a definition is almost superfluous. Fountain pens, telephones, phonograph records, buttons, rayon, and tires are such familiar objects in our daily life that the ability to recognize a plastic material is almost as well developed as the nearly instinctive recognition of a metallic object.

The term "plastic" is frequently used to mean the material both before and after the forming operation. This does not mean that all finished plastic objects are necessarily made from plastics any more than a solid needs to be formed from a solid. A plastic object frequently is in the liquid state or in solution before and during the forming operation. On the other hand, finished products made from plastic materials are frequently referred to as plastics, although in their final form they can no longer be formed by heat and pressure. This confusion in the use of the word has led to the general implication of a generic meaning in the word plastic. Since this general usage has determined the meaning of the word, plastics are relatively high molecular weight organic materials that have been or can be formed by heat and pressure or pressure alone and will retain their shape under normal conditions of temperature and pressure.

It is possible to define the term "resin" somewhat more precisely, yet here again clarity is usually sacrificed when an attempt is made to be too precise. Resins are the raw materials from which plastics are made, and

yet they have many other extremely important uses. They are usually organic compounds of high molecular weight, but are not a specific compound in the true sense of the word. The synthetic resins are frequently polymers of a recurring structural unit called a "monomer," but do not form a specific compound because the number of recurring units in each molecule or particle is not a constant. Many of the naturally occuring resins, such as shellac, *are* mixtures of high molecular weight compounds of complex structure and as such would have to be classified as exceptions to the foregoing concept.

The situation is also complicated by the fact that not all organic high polymers are resins. Cellulose, for example, is not ordinarily considered a resin, although in some specific applications it is a borderline case. The resinous character of high molecular weight organic compounds is best designated by their use. They are the essential base material in all plastics and in most coating materials and adhesives. In order to make a finished plastic article it may be necessary to mix pigments, fillers, plasticizers, and other modifiers with the resin before molding, but it is the resin that holds the other materials together, and it is the resin that is the basic ingredient. Likewise in a coating it is the resin that forms the coat even though pigments or fillers may comprise most of the actual volume. Resins are also the fiber-forming material in the production of rayons.

This concept of resins includes rubber, cellulose derivatives, and proteins—materials that are usually carefully distinguished from resins and considered separately. They have become individual materials in their own right because the quantities involved in their industrial applications are so large and their chemistry is so complex that they warrant a separate consideration. However, rubber has many of the properties of a resin and differs less from many of the synthetic resins than they do among themselves. Cellulose, when used in the form of cotton or wood products, is obviously not a resin, but many of its derivatives are. Cellulose acetate is one of the best known resins in the plastics industry. There has been a tendency to call cellulose acetate a resin when used as a plastic and to call it something else when it is spun into a rayon, even though in both cases the cellulose acetate might have come from the same storage bin. There is no sound reason for this distinction. The spinning process is a special method of forming a plastic material in which a solvent is used to aid in plasticizing the resin and, in the case of cellulose acetate, differs from the continuous extrusion of plastic shapes in degree only. Proteins are not so simply classed as resins. Obviously there are proteins that are not resins in any sense of the word. Yet proteins do not differ from synthetic resins any more than does shellac, which is one of the best-known natural resins. For this reason some protein materials and their derivatives are included as resins.

This broad concept of resins or resinous character includes a wide range

of products. However, there is a distinct relationship between the individual resins that is better understood by a broad coverage of the entire field. The specific resins that will be discussed are included in the following classification.

Classification of Resins.—A classification of the various types of resins aids in the discussion of their production and properties. The following classification is based on sources of raw materials, on types of polymerization reactions, and, in the case of the synthetic rubbers, on specific properties. The classification is limited to those resins in commercial use and production.

I. Resins derived from high molecular weight natural products
    A. Natural products
        1. Fossil and plant resins
        2. Rosin
        • 3. Shellac
        4. Lignin
    B. Cellulose derivatives
        1. Regenerated cellulose
            a. Viscose
            b. Cuprammonium
        2. Cellulose esters
            a. Nitrate
            b. Acetate
            c. Mixed
            d. Propionate
        3. Cellulose ethers
        4. Oxidized cellulose
    C. Rubber derivatives
        1. Chlorinated rubber
        2. Rubber hydrochlorides
    D. Proteins and protein derivatives
II. Resins formed by condensation reactions
    A. Phenol-aldehyde resins
        1. Phenol-formaldehyde
        2. Phenol-furfural
        3. Resorcinol-formaldehyde
    B. Amide-aldehyde resins
        1. Urea-formaldehyde
        2. Melamine-formaldehyde
    C. Aniline-aldehyde resins
    D. Polyesters
        1. Alkyds
        2. Unsaturated
    E. Polyamides
III. Polyethenic compounds
    A. Polyethylene
    B. Polyisobutylene
    C. Polyvinyl acetate and its derivatives
        1. Polyvinyl alcohol
        2. Acetals

      D. Polyvinyl chloride
      E. Polyvinyl copolymers (chloride-acetates)
      F. Polyvinylidene chloride
      G. Polystyrene and polychlorostyrene
      H. Acrylic polymers
      I. Polyvinyl ethers
      J. Polyvinyl ketones
      K. Divinyl polymers
      L. Coumarone-indene copolymers
      M. Fumaric polymers

IV. Silicones
V. Rubber and synthetic rubbers.
      A. Rubber
      B. Butadiene copolymers
           1. With acrylonitrile
           2. With styrene
      C. Chloroprene polymers
      D. Isobutene-diolefin copolymers
      E. Polysulfide rubbers

This classification is arbitrary in some respects. Perhaps the most carefully drawn distinction is in class V. Only vulcanizable polymers have been classed as rubbers. It should be realized that there are many other resins that can be made into a rubberlike plastic that may be superior to either natural or synthetic rubber for specific uses requiring elasticity. However, nearly all the materials possessing rubberlike properties also have many other uses as synthetic resins and should be considered as one entity.

This classification is very useful as an aid in remembering the various resins and some of their fundamental properties. It should be referred to carefully in connection with the later text, since the individual plastics are taken up in this order.

THE POLYMERIZATION REACTION

The chemical reactions that produce resins have been generally termed "polymerization reactions," regardless of whether the reaction is performed by nature or in the reaction kettles of a chemical plant. Actually, there are two different types of reactions that play a particularly important role in the field of synthetic resins, but the word "polymerization" is frequently used to mean the building up of large molecules from smaller ones, into linear chains or a three-dimensional network, without regard to the reaction involved. The formation of higher molecular weight substances from small units is classified into two distinct and carefully defined reactions—condensation and polymerization. Polymerizations are defined as those reactions which yield a product that is an exact multiple of the original molecule. In other words, the percentage chemical composition remains the same. A typical example of this reaction is the formation of vinyl and divinyl acetylene from acetylene.

This type of polymerization has been termed "addition polymerization."

$$2CH{\equiv}CH \longrightarrow CH_2{=}CH{-}C{\equiv}CH$$
$$3CH{\equiv}CH \longrightarrow CH_2{=}CHC{\equiv}CCH{=}CH_2$$
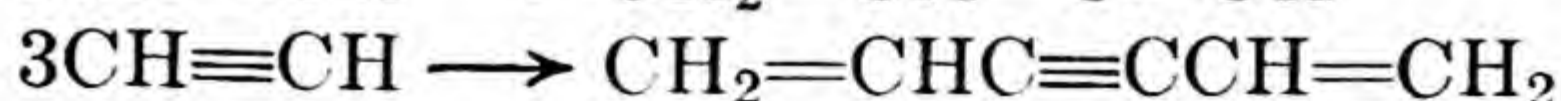
Condensations, on the other hand, take place by the uniting of two or more molecules with the loss of a small molecule. Water is usually split off. An example of this reaction is the formation of ethyl acetate from acetic acid and ethyl alcohol, or the first step in the formation of a polyester resin in which glycerine and phthalic acid are combined.

$$\overset{COOH}{\underset{COOH}{\bigcirc}} + CH_2OHCHOHCH_2OH \longrightarrow$$

$$\overset{COOCH_2CHOHCH_2OH}{\underset{COOH}{\bigcirc}} + H_2O$$
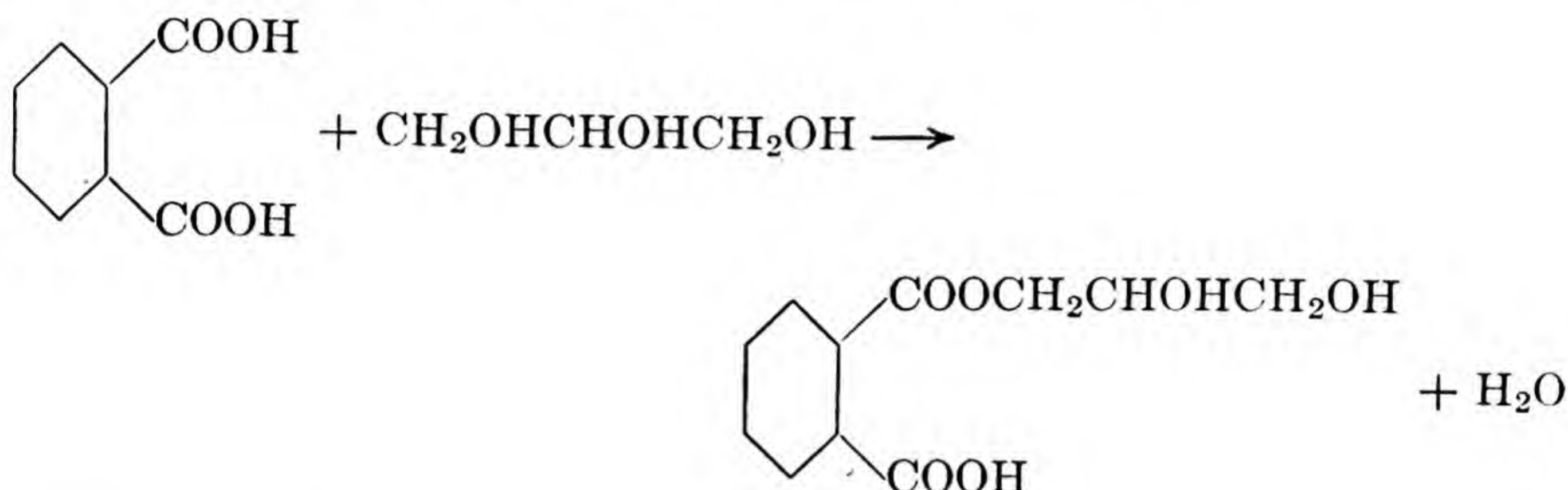
Polymerization is an important reaction in the synthetic resin industry as well as in petroleum technology. It is interesting to note that the process of polymerization has as its basis those troublesome reactions that bothered the organic chemist in the early days of synthetic organic chemistry. Derivatives of high molecular weight were often obtained through some uncontrollable side reaction and the products labeled as "tars" or "unidentified compounds." Whenever this took place, it was an immediate signal that the original synthesis would either have to be revised or abandoned. The polymeric derivative was apparently non-crystalline, and, since there was no simple method known for the determination of the molecular weight, an empirical formula was assigned followed by an n denoting an unknown degree of polymerization. The same method of designating polymers is used at present. Rubber can be expressed as $(C_5H_8)_n$ and cellulose as $(C_6H_{10}O_5)_n$.

Although the use of n to designate the degree of polymerization amounts to a confession of ignorance, it is probably the best way of expressing the facts, as none of the natural or synthetic highly polymerized compounds have a definite molecular weight. They are composed of recurring units, but the degree of polymerization, n, or the number of times the units recur, is not a constant but varies between wide limits. It is true, however, that careful control and choice of conditions of preparation or treatment will generally yield a product having about the same average degree of polymerization.

There are two basic types of polymers. In one case the mechanism of

polymerization builds up a long linear chain of polymerized monomers. Styrene forms a typical polymer of this type.

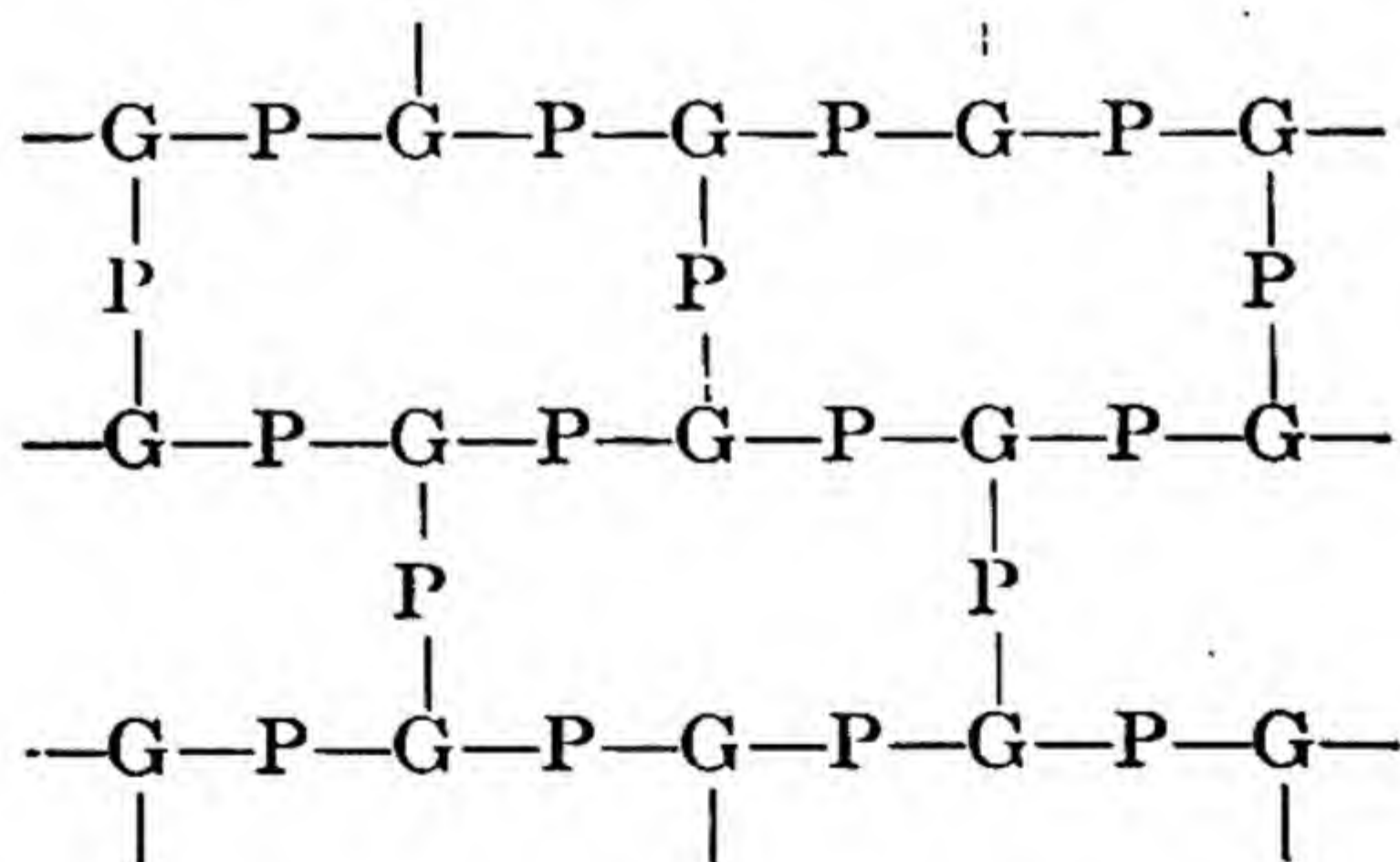$$CH{=}CH_2 \quad\longrightarrow\quad {-}{-}CHCH_2{-}\left[{-}CHCH_2{-}\right]_n {-}CHCH_2{-}{-}$$
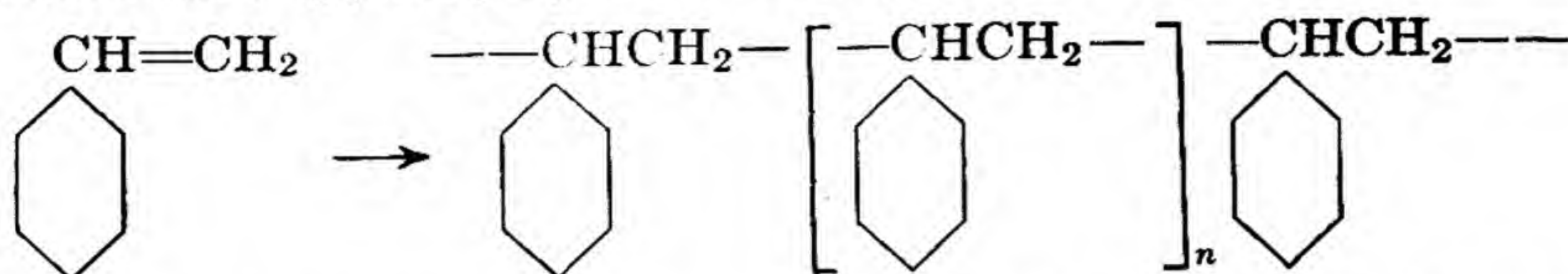
The ends of the chains cannot be accounted for directly. Cyclic compounds are not probable because of the size of the chains, but the end valences may be satisfied by the absorption of solvent, water, or catalyst or by internal partial valences. In the case of polymerized polystyrene, there is no possibility of direct cross linkage from chain to chain by primary valences. All the primary valences are satisfied; if any association between the linear chains does occur, it must be accomplished by secondary forces.

A completely different type of molecular polymeric structure can be built up in which the linear chains may be linked together at certain points with the formation of a three-dimensional network design. The molecular structure of this type of polymer is very compact and complex. The diamond probably represents the perfect, three-dimensional structure. Any diamond is one single molecule in which each carbon atom is connected to four surrounding carbon atoms by four valence bonds.

The three-dimensional type of polymeric structure may be visualized in the reaction of glycerol and phthalic acid to yield the glycerol phthalate polyester. If we let —G— represent glycerine and —P—, phthalic acid, the resulting polymerization can yield a compound of the following structure:

$$
\begin{array}{c}
{-}G{-}P{-}\overset{\mid}{G}{-}P{-}G{-}P{-}G{-}P{-}G{-} \\
\mid \qquad\qquad \mid \qquad\qquad \mid \\
P \qquad\qquad P \qquad\qquad P \\
\mid \qquad\qquad \mid \qquad\qquad \mid \\
{-}G{-}P{-}G{-}P{-}\overset{\mid}{G}{-}P{-}G{-}P{-}\overset{\mid}{G}{-} \\
\mid \qquad\qquad \mid \\
P \qquad\qquad P \\
\mid \qquad\qquad \mid \\
{-}G{-}P{-}\overset{\mid}{G}{-}P{-}G{-}P{-}\overset{\mid}{G}{-}P{-}G{-} \\
\mid \qquad\qquad \mid \qquad\qquad \mid
\end{array}
$$

Thus molecular growth may occur in several directions. The growth is, of course, three-dimensional rather than two-dimensional, as shown in the illustration, and does not have the degree of regularity implied in this idealized representation of the structure.

These two types of polymers characterize two entirely different classes

of resins and plastics. The linear or chain polymers are thermoplastic; *i.e.*, they soften with heat and are permanently fusible. In addition, they have varying solubilities in organic solvents. Thermosetting resins, on the other hand, once the three-dimensional structure is obtained, do not soften appreciably with the application of heat and are not appreciably soluble if the three-dimensional structure is extensive. They exhibit the property of swelling in organic solvents, resembling the behavior of starch in hot water. The degree of swelling is an indication of the extent of cross linkage or three-dimensional structure. It should be realized that these structures are idealized and that there are many intermediate structures in which branching of the chains or a moderate amount of cross linkage exists. Polymers of this type have properties intermediate between the two extremes.

There are four general types of structure that have been recognized, although the distinction between adjacent types is one of degree only, rather than of completely different structure.

1. *Straight-chain Polymers.*—This structure is composed of long linear chains without branching or cross linkage; best visualized as a bundle of threads, the threads may be straight, kinked, or spiral in form. Polystyrene belongs to this general type of polymer. Properties are those of a typical thermoplastic material.
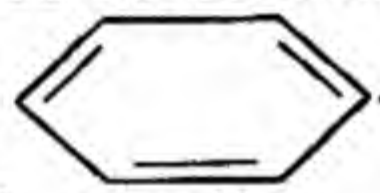
2. *Branched-chain Polymers.*—This structure can be compared to a branch or treelike arrangement in which side chains fork out from a parent linear chain. The amount of branching is extremely important in its effect on properties. In general, solubility is reduced, softening point increased, and workability reduced with increased branching. Butadiene polymers are usually branched.

3. *Moderately Cross-linked Polymers.*—Again there is a wide variation in effect, depending on the number of cross links between the linear chains. This type of structure is characteristic of elastomers or elastic polymers in which there is enough cross linkage to prevent the slippage of linear chains past one another, but not enough to produce a rigid structure. However, the polymer is no longer thermoplastic. Butyl rubber has this characteristic structure.

4. *Highly Cross-linked Polymers.*—A high amount of cross linkage is characteristic of thermosetting resins where the structure can be compared with a tire chain in which the cross chains are the cross links between the two longer outside chains. The total structure is, of course, continuous and forms a network that can be visualized as a pattern similar to the outline of mortar in a brick wall. The actual structure is not nearly so regular as implied by this idealized picture, but a large amount of cross linkage always exists. Phenol-formaldehyde resins are highly cross-linked thermosetting polymers.

As mentioned previously, these structures are built up by two main reactions. The mechanism by which these two reactions proceed is quite different, but both of them require polyfunctionality of the reacting molecules. In the case of the typical addition polymerization, bifunctional monomers containing at least one double bond react to build up linear polymers. In this case, the easy shift of the second-order electrons of the double bond to the ends of the molecule causes it to become and remain bifunctional.[1] The polycondensation reaction takes place between two or more functional groups capable of reacting, which are attached to each molecule. Actually, this type of linkage need not take place by means of condensation reactions alone, since there are many other methods by which functional groups may react. Practically, however, the polycondensation reaction between functional groups and the addition polymerization of unsaturated monomers are the only two important methods of building up high molecular weight compounds in the field of resins.

Addition Polymerization.—Unsaturated compounds differ greatly in their tendency toward polymerization. The simple olefinic hydrocarbons are difficult to polymerize even under extreme conditions, but will react in the presence of catalysts. Thus ethylene is made to polymerize to polyethylene, but catalysts and very high pressures are required. The olefinic monomer can be made much more reactive by (1) substitution, which confers polarity on it, and (2) its participation in a semibenzenoid conjugated system or in a potentially conjugated aliphatic system.[2]

Vinyl chloride, $CH_2=CHCl$, and vinylidene chloride, $CH_2=CCl_2$, are typical examples of the first case, in which a high degree of polarity is obtained by chlorine substitution and the monomers react readily to build up high polymers. The ease with which the aromatic-aliphatic conjugated system polymerizes is typical of styrene, $\langle\!\!\!\bigcirc\!\!\!\rangle$—$CH=CH_2$, and the polymerizability of acrylic esters and acrylonitrile,

$$CH_2=CHC=O \qquad\qquad CH_2=CHC\equiv N$$
$$\underset{\displaystyle OR}{\big|}$$
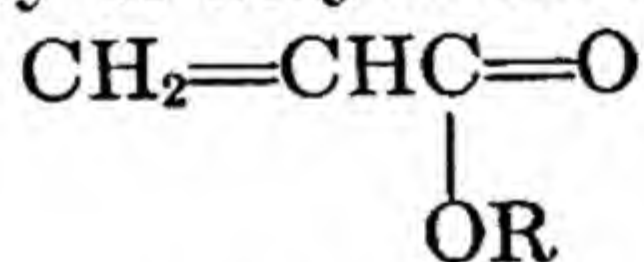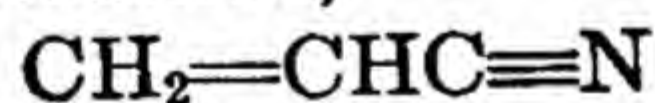
Acrylic esters   Acrylonitrile

are examples of the reactivity of potentially conjugated systems.

Diolefins such as butadiene, in which the bonds are arranged in a conjugated system, polymerize readily. Polar substituents tend to enhance polymerizability, so that 2-chlorobutadiene polymerizes more readily than does butadiene.

Addition-polymerization reactions proceed in three distinct phases: (1) the activation of the monomer, (2) the propagation of the chain, and (3) the cessation reaction or termination of the chain. Nuclei of poly-

[1] HOHENSTEIN, W. P., *Polymer Bull.*, 1, 60 (1945).
[2] WHITBY, G. S., *Chem. Eng. News*, 22, 1571 (1944).

merization are first formed, and these nuclei add on monomeric units as though additional links were being added to a chain. The ends of these chains retain the activity of the nucleus until deactivated by a cessation reaction. These steps may be indicated schematically if M designates an unactivated monomer. Activation is indicated by an asterisk.

$$M + \text{energy} = M^*$$
$$M^* + (m-1)M = [M]_n^*$$
$$[M]_n^* - \text{energy} = [M]_n$$
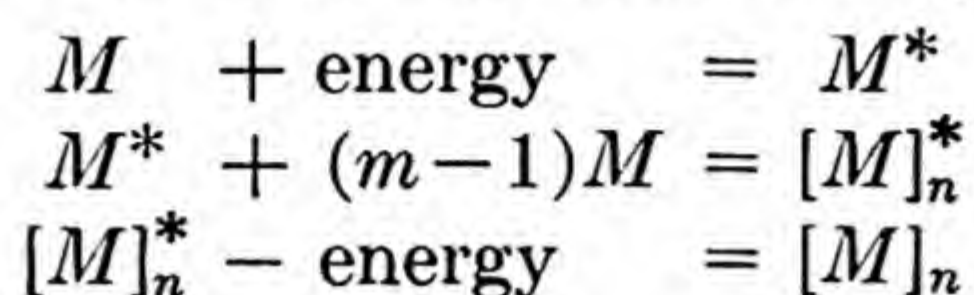
An olefine molecule may be activated by absorbing a quantum of light or, thermally, by a collision, and thus may be converted into an active nucleus. Catalysts such as peroxides, ozone, and metallic halides have the effect of diminishing the energy of activation, although this may not be the actual mechanism by which they promote polymerization. The effect of these catalysts is shown by their catalytic action on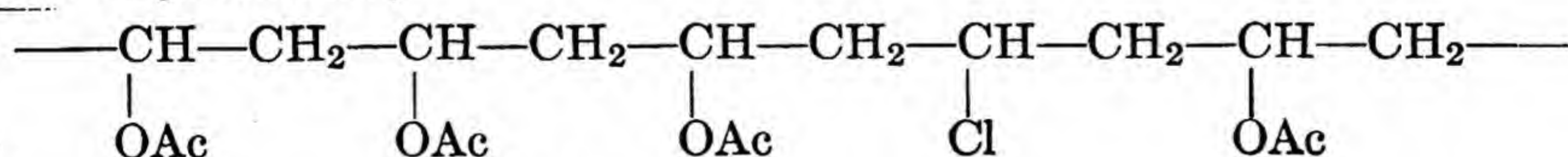 polymerization processes. The activated molecules act as nuclei for addition polymerization. Monomers add on to the nucleus readily at a much lower energy level, so that, once started, the propagation reaction continues readily since the heat liberated by the reaction is usually ample to supply the necessary energy.

Chain growth stops when the active molecule collides with the wall of the reactor or with other types of molecules. Aromatic hydroxy compounds are effective inhibitors of addition polymerization in the presence of oxygen. Hydroquinone and phenol will effectively prevent polymerization. They are frequently added to monomers to prevent polymerization during storage since they are easy to remove by a simple caustic wash before polymerization is carried out.

It is possible for a growing primary valence chain to lose its energy quantum to a monomeric molecule, thereby becoming deactivated, while the monomer now acts as a new nucleus. The course of polymerizarion differs according to reaction conditions. The presence of many nuclei may lead to the formation of short chains; few nuclei and the absence of all impurities leading to the interruption of the chains tend to produce longer chains.

Copolymerization.—Copolymerization takes place when two different monomers are capable of entering the growing chains at relatively the same energy level and rates. Such polymers may contain several recurring units of the same monomer, interrupted by occasional units of the second type. A common example is the copolymer obtained from vinyl acetate and vinyl chloride,

$$-\!-\!-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-\!-\!-$$
$$\quad\ |\qquad\quad |\qquad\quad |\qquad\quad |\qquad\quad |$$
$$\quad OAc\quad\ OAc\quad\ OAc\quad\quad Cl\quad\quad OAc$$

in which OAc represents the acetate group.

If two or more different monomers are copolymerized, they may either combine in a random manner or a preferred order of entry into the chain may prevail. Recent investigations[1] indicate that the distribution of the monomeric units along the chain is entirely random.

The ratio of monomers in commercial copolymers varies widely. In some, the ratio is of the same order of magnitude. In others, one is only a per cent or two of the other. Variations in properties produced by different types and quantities of copolymers are extremely important. In some cases, they have converted a laboratory curiosity into a valuable commercial product. There are cases known in which monomers that will not polymerize with themselves (homopolymerization), even under the most drastic conditions, will readily copolymerize with another species. Copolymerization greatly increases the number of possible polymeric products that can be made from readily available monomers and offers tremendous possibilities for the production of resins best suited for particular applications.

Copolymerization is often resorted to in order to impart to a resin the good qualities of two different polymer species. Rarely is this accomplished by a physical mixture of the two polymers. The result of copolymerization is often referred to as "internal plasticization," which is superior to an attempt to modify the plastic properties of a polymer by the use of a high-boiling-point external plasticizer.

Methods of Carrying out Addition Polymerizations.—Polymerization may take place in a liquid monomer, in solution, in an emulsion, or in a suspension. If polymerization occurs in the liquid monomer itself, the entire contents of the vessel gradually polymerize and form a solid mass at room temperature. In many cases the polymer is soluble in the monomer and the mass becomes more and more viscous until it finally solidifies. Methyl methacrylate and polystyrene are examples. This is known as "bulk," or "mass," polymerization and is of particular importance in the so-called "casting method," in which the liquid monomer is solidified by polymerization. Usually it is difficult to remove the heat of polymerization in a bulk reaction, particularly if agitation must be avoided, because of the viscous stage that must be passed through before solidification. This method of polymerization is not suitable for some types of monomers. The acrylic acids form polymers that are only slightly soluble in the monomers and settle out as white deposit. Polymerization proceeds from the bottom upward until a white solid cake is formed, yielding polymers of low molecular weight. There are many variations; acrolein, for example, polymerizes to a spongy white mass that swells in its own monomer.

Polymerization in solution removes all difficulty of heat removal and

[1] REHNER, J., JR., *Ind. Eng. Chem.*, **36**, 46 (1944); ALEKSEVA, E. N., and R. M., BELITZKAYA, *Rubber Chem. Tech.*, **15**, 693 (1942).

control, but the presence of a solvent usually slows down the reaction considerably and produces polymers of low or moderate molecular weights since the solvent molecules can act as chain interrupters. In addition, it is difficult to strip off the last traces of solvent from the extremely viscous, sticky polymer, and any traces of solvent remaining may have a considerable effect on the properties of the resin.

Polymerization in emulsion and in suspension actually differ only in the size of the suspended droplets, although this difference produces important variations in obtaining the final product. In emulsion polymerization, a colloidal dispersion of the monomer in water is obtained by the use of soap or other emulsifying agents and stabilizers. Catalysts and modifiers are also added. At the end of the reaction, a latex of colloidal polymer suspended in water is obtained which must be coagulated before it can be filtered off, washed, and dried.

In dispersion, or bead, polymerization, no attempt is made to obtain a true emulsion. In fact every effort is made to avoid extremely small-sized droplets. Liquid globules of monomer are kept in suspension by just the correct amount of agitation, a low ratio of water to monomer, and special stabilizers.[1] The spherical globules range in size from 0.5 to 5.0 mm., so that the coagulation step is not necessary to produce a filterable suspension after polymerization. Bead polymerization is a very desirable method for preparing a product for molding. The size of the beads can be controlled within narrow limits by the proper selection of conditions of temperature, dispersing agent, and catalyst concentration, and thus a product of uniform apparent density is obtained. Methyl methacrylate, styrene, and vinyl acetate lend themselves to this method of polymerization.

CONDENSATION

Condensation reactions require the presence of at least two functional groups on all monomers for the formation of high molecular-weight compounds. Usually two different monomers are employed, each with functional groups capable of reacting with the other. Thus dibasic acids react with dihydric alcohols to give polyesters, or dehydration occurs by the loss of hydroxyl and hydrogen to form a new bond between a methylene group and an aromatic ring.

Condensation polymers may be either thermoplastic or thermosetting. Normally, thermoplastic resins result if bifunctional molecules react that are not capable of reacting if any other manner. Polyfunctionality is required for the formation of thermosetting compounds. This may be obtained with molecules that contain three or more functional groups, or it may be obtained by reactions with active hydrogen atoms.

[1] HOHENSTEIN, W. P., *Polymer Bull.*, 1, 14 (1945).

If two different functional groups are contained in the same molecule, the reaction proceeds to form a linear molecule composed of identical recurring groups similar to addition polymers.
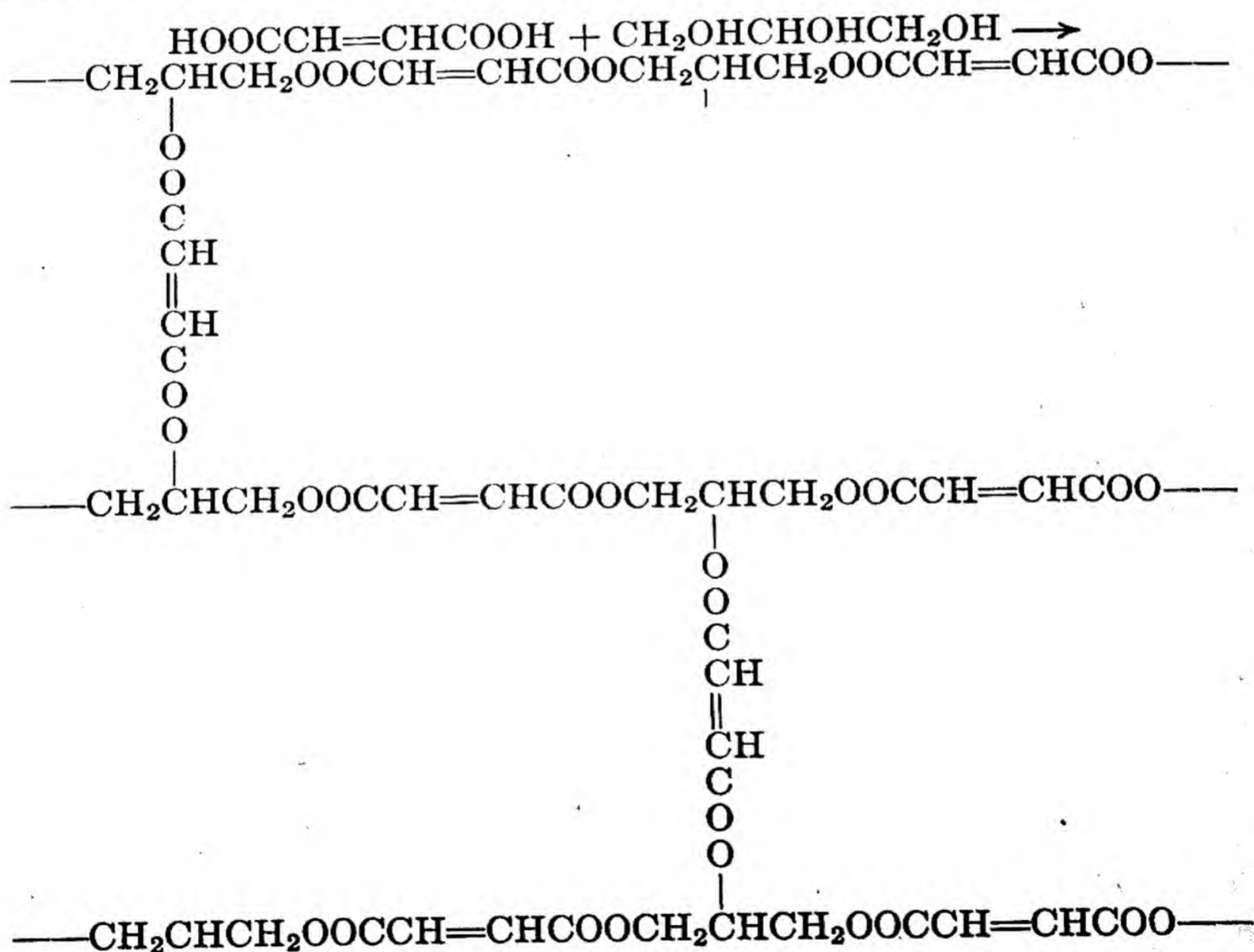
$$HOCH_2CH_2CH_2CH_2COOH \longrightarrow [\text{---}CH_2CH_2CH_2CH_2COO\text{---}]_n$$
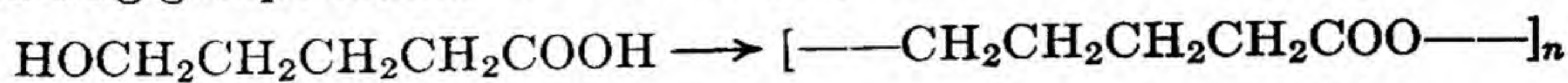
A linear polymer will also result if the different functional groups are present on different monomers, as in maleic acid and ethylene glycol.

$$HOOCCH{=}CHCOOH + CH_2OHCH_2OH \longrightarrow$$
$$[\text{---}CH_2CH_2OOCCH{=}CHCOO\text{---}]_n$$
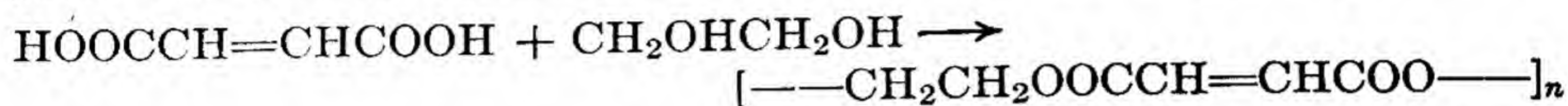
The recurring unit is now composed of residues derived from two different monomers and, in some respects, might be compared with a copolymer formed by addition polymerization except that a regular alternating, rather than a random, arrangement is present.

If one species contains more than two functional groups, a highly cross-linked thermosetting structure can be obtained, such as that obtained by condensing maleic acid and glycerine.

$$HOOCCH{=}CHCOOH + CH_2OHCHOHCH_2OH \longrightarrow$$
$$\text{---}CH_2CHCH_2OOCCH{=}CHCOOCH_2CHCH_2OOCCH{=}CHCOO\text{---}$$

$$
\begin{array}{c}
| \\
O \\
O \\
C \\
CH \\
\| \\
CH \\
C \\
O \\
O \\
| \\
\end{array}
$$

$$\text{---}CH_2CHCH_2OOCCH{=}CHCOOCH_2CHCH_2OOCCH{=}CHCOO\text{---}$$

$$
\begin{array}{c}
| \\
O \\
O \\
C \\
CH \\
\| \\
CH \\
C \\
O \\
O \\
| \\
\end{array}
$$

$$\text{---}CH_2CHCH_2OOCCH{=}CHCOOCH_2CHCH_2OOCCH{=}CHCOO\text{---}$$

This structural formula represents a highly idealized structure but does indicate how cross linkages can be formed to produce thermosetting resins.

Another type of condensation reaction is, in reality, a combination of two reactions, the first of which forms an intermediate that is either bi- or polyfunctional. The intermediate is then capable of condensing to produce a polymer. This reaction is typical of those polymers made from phenol and formaldehyde in which the first reaction produces ortho- or para-methylol phenol followed by a condensation of this intermediate.
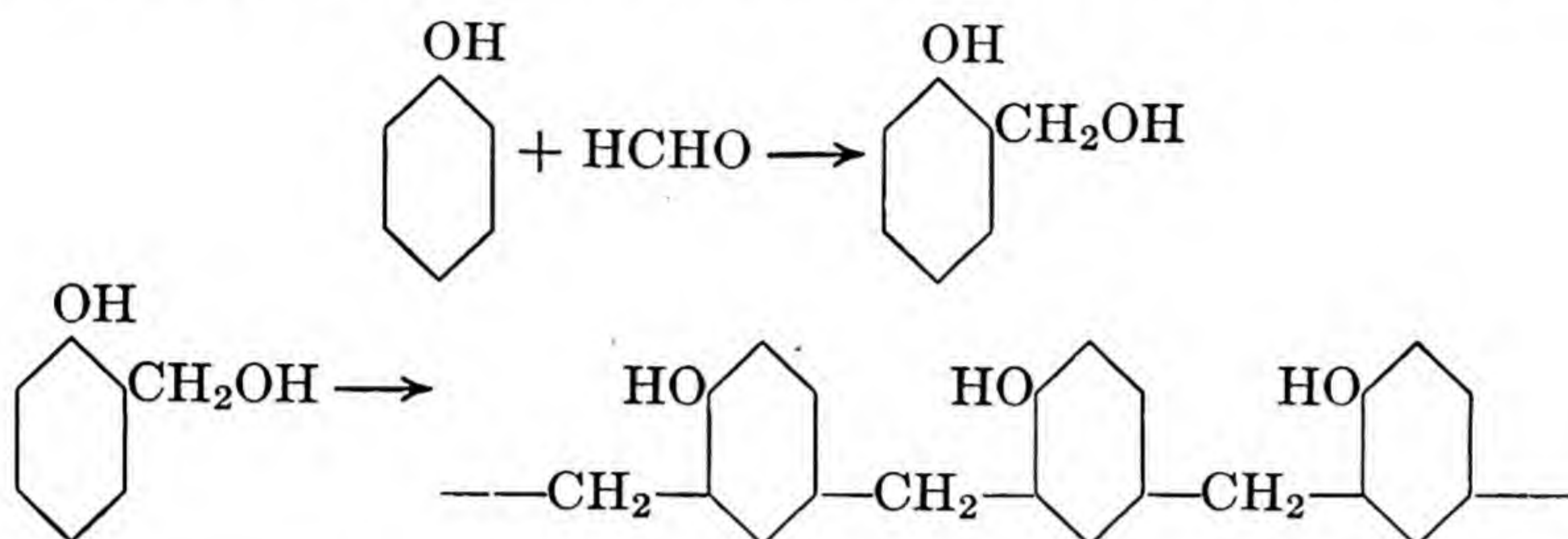
Additional formaldehyde can react either forming polymethylol phenols and thus producing polyfunctional molecules, or it can establish cross linkages by reacting with the benzene rings in the chains. In either case, a thermosetting resin results, and these particular polymers are the most widely used thermosetting resins.

The condensation reaction differs from addition polymerization in that a small molecule, usually water, is split off during the reaction. Most of the water formed must be removed before the formation of the final plastic article, and the methods by which it is removed must be considered from the time the reaction starts until the final product is formed.

Polycondensations are relatively slow stepwise reactions. The intermolecular reactions between the different functional groups are repeated many times to build up a high molecular-weight compound. The mechanism by which the reaction proceeds is similar to the same type of reaction between simple monofunctional groups. Depending on the type of resin formed, polycondensations may proceed by esterification, etherification, or dehydration reactions in which the actual mechanism by which new carbon-to-carbon bonds are formed is similar to the formation of simple esters, ethers, amides, etc.

In general, these reactions either require no catalysts or are strongly catalyzed by acid or basic water-soluble catalysts. Relatively higher temperatures are employed during the reaction and have much the same effects as on reactions between monofunctional monomers. Since water is eliminated, it is customary to employ vacuum either throughout the reaction or during the later stages. This dehydration produces a viscous thick resin that must be removed from the reaction kettle before actual gelation takes place. If a thermosetting resin is being produced, care must

be employed to restrict the extent of the reaction in the kettle, since the final product would be a solid resin that could be removed only with great difficulty and would not be suitable for further processing.

The requirements of fusibility and sufficient reactivity for further processing, particularly for the final "setting-up" reaction in the mold, result in the production of a resin that is only partly polymerized as it comes from the kettle. The desired degree of polymerization is obtained by heating the solid resin, by adding more of one of the monomers, or by catalysts. If the thermosetting resin is to be used in a molding powder, the final polymerization or "cure" is produced by heating the mold in the final molding operation. In any application, the last stages of the reaction that produce enough cross linkages to give the resin a typical thermosetting structure must be obtained after final forming or application, since it cannot be readily formed or worked except by machining after this stage is reached.

There is some evidence[1] that the molecules formed in the early stages of the reaction have relatively low molecular weights. These molecules form nuclei for further growth, much as the activated chains continue to grow in addition polymerization, except that the growth forms highly branched chains emanating in all directions. This process continues until the amount of available reactants remaining terminate the growth. At this point, relatively large macromolecules, more or less spherical in shape, exist. Barkuff and Carswell postulate that this structure is characteristic of phenolic resins in which the reaction has been carried to the point where the resin is ready for the final cure. The molding operation then produces cross linkage between the macromolecules, and a rigid three-dimensional structure is produced.

MOLECULAR WEIGHTS, DEGREE OF POLYMERIZATION, AND EFFECT OF STRUCTURE

High polymers have molecular weights ranging from twenty thousand to several hundred thousand and, in some cases, over a million. The determination of molecular weights of this magnitude is extremely difficult since the application of the usual molecular-weight determinations requires the use of very dilute concentrations. With high molecular-weight materials, however, finite concentrations are usually required to produce measurable effects. Carefully worked out techniques have been developed that give good results of sufficient accuracy so that the results furnish a reliable indication of the size of the molecules, although the absolute accuracy may leave something to be desired.

One method[2] involves the determination of the osmotic pressure of a

[1] MEGSON, N. J. L., *Trans. Faraday Soc.* (1935); BARKUFF, R. A., and T. S. CARSWELL, *Ind. Eng. Chem.*, 36, 461 (1944).

[2] MARK, H., *Am. Scientist*, 31, 101 (1943).

high polymer in dilute solution.   If 1 g. of a high polymer is dissolved in 1 l. of solvent and the osmotic pressure is measured by the height h of a column of the solvent in millimeters, then the molecular weight M of the material is given by the formula

$$M = \frac{240,000}{h} \tag{1}$$

This formula is a good approximation only as long as the density of the solvent is not too far from 1.   Thus a material, such as cellulose acetate, with a molecular weight of 24,000 produces a solvent column of 10 mm., which is relatively easy to measure.   On the other hand, a high polymer like native cotton, with a molecular weight of 500,000, gives a pressure difference of less than 0.5 mm., which is difficult to measure by this method.

In another method for determining the molecular weight of high polymers, the ultracentrifuge is employed.   The diluted solution of a high polymer is subjected to the strong centrifugal field produced (up to 1 million times gravity), and the rate and the equilibrium of sedimentation are observed.   Knowing the density of the dry polymer and the solvent, the molecular weight of the former can be calculated.   This method is effective even for the highest molecular weights and has been used extensively for studies on all important high polymers.[1]

Many high polymers are chains built up of repetitive identical units. For example, cellulose is composed of $C_6H_{10}O_5$ groups, rubber by C_5H_8 residues, nylon by adipic acid and hexamethlenediamine units, etc.   In these examples, the groups at one or both ends of the chains have a unique chemical structure, differing from the groups in the middle of the chain.

Thus each cellulose chain has a potential aldehyde group $\left[\begin{array}{c} H \\ | \\ --COH \\ | \\ -O \end{array} \right]$, each

rubber chain has a double bond ($H_2C{=}CH{-}{-}$) on one end.   These functional groups can often be determined by neutralization or chemical reactions.   Knowing their number, n, in a given amount of the high polymer under consideration and knowing the molecular weight, M_0, of the monomeric unit, the molecular weight of the polymer can be determined with the aid of the formula

$$M = \frac{A}{n} M_0 \tag{2}$$

where A is 6×10^{23}.

[1] MEYER, K. H., "Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, 1942.

Viscosity determinations are probably the most widely used method for determining approximate molecular weights. The simplest relationship is that proposed by Staudinger,[1] which relates the ratio of specific viscosity η_{sp} to concentration and the average molecular weight.

$$\left[\frac{\eta_{sp}}{c}\right]_c = KM \tag{3}$$

The specific viscosity is defined by the equation

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 \tag{4}$$

where η = viscosity of solution
η_0 = viscosity of pure solvent

The absolute accuracy[2] of this method is in doubt, but wide experience with the method and large accumulations of data have enabled most research and control laboratories to correlate the results of viscosity determinations to give very useful approximations of the average molecular weight.

Various types of polymers have been investigated with the methods just described, and the results of the different methods check fairly satisfactorily. Table 1 indicates the approximate order of magnitude of the molecular weights and degree of polymerization of certain high polymers.

Cellulose in native cotton, rayon, or wood has a polymerization degree as high as 2,000 to 3,000; similar figures have been found for native rubber and for some synthetic polymers, such as polyisobutylene, polystyrene, and polyvinyl chloride. For many purposes the high degree of polymerization of the original material is reduced or degraded and stabilized at some lower figure to facilitate the processing of mixtures, compounds, or solutions. Thus it can be seen from Table 1 that, for the convenience of spinning or casting solutions of cellulose or its derivatives, the raw material is bleached cotton linters or purified wood pulp, both having degrees of polymerization around 1,000. The cellulose chains in the final products such as rayon or cellophane have an average length of only 300 to 600 glucose units, a degree of polymerization that corresponds to molecular weights of 50,000 to 100,000. Similarly, native rubber is degraded to a degree of polymerization below 1,000 by milling it in the presence of oxygen in order to facilitate the incorporation of fillers, plasticizers, and vulcanization ingredients.

It is sometimes possible to control the polymerization process in such a way that the degree of polymerization of the resulting product is controlled.

[1] STAUDINGER, H., "Die hochmolekularen organischen Verbindungen," Verlay Julius Springer, Berlin, 1932.
[2] HUGGINS, M. L., *Ind. Eng. Chem.*, 35, 982 (1943).

If this is the case, different types of the same polymer are produced for different purposes, such as for coating, extrusion, or injection molding.

In addition to the degree of polymerization of a high polymer, the distribution of the various chain lengths has an important effect on the properties of the product. All natural and synthetic polymers are heterogeneous in respect to the lengths of the chains that they contain. All polymers are a mixture of chains having different degrees of polymerization, so that the figures of Table 1 can be considered only as average values.

TABLE 1.—MOLECULAR WEIGHTS AND POLYMERIZATION
DEGREES OF HIGH POLYMERS

Material	Molecular weight	Polymerization degree
Native cellulose in cotton, ramie, or wood...	300,000–500,000	2,000–3,000
Cellulose in bleached cotton linters........	150,000–230,000	1,000–1,500
Cellulose in purified wood pulp...........	120,000–200,000	800–1,200
Regenerated cellulose in rayon...........	75,000–100,000	500– 600
Regenerated cellulose in cellophane........	50,000– 60,000	300– 400
Native rubber in Hevea latex............	140,000–210,000	2,000–3,000
Rubber after being milled in air.........:.	55,000– 70,000	800–1,000
Nitrocellulose used for molding...........	400,000–700,000	1,500–2,500
Nitrocellulose used for extrusion..........	150,000–300,000	600–1,200
Nitrocellulose used for coatings..........	50,000–100,000	200– 400
Polystyrene for injection molding.........	60,000–500,000	1,200–6,000
Polystyrene for coating.................	80,000–120,000	800–1,200
Polyvinyl chloride......................	250,000	3,000
Polyisobutylene.......................	120,000–200,000	2,000–3,000
Polyhexamethylene adipamide (nylon).....	16,000– 32,000	150– 300

MARK, H., *Am. Scientist*, **31**, 104 (1943).

A fractional-precipitation method has been employed for the determination of molecular weight distribution.[1] When applied to a cellulose acetate-butyrate material, a 2 per cent solution in acetone was prepared and precipitation into fractions was carried out with successive additions of water. The higher molecular-weight species precipitated first. From viscosity measurements on the various fractions, a molecular weight distribution curve was plotted. The precipitation method can be used in some cases to determine whether a true copolymer is attained when two monomers are polymerized together, or whether it is a mechanical mixture of the two individual polymers.

Figure 1 is the usual type of differential-distribution curve, which illustrates the variation in the chain lengths. This curve shows that the most frequent degree of polymerization in the sample is around 2,500 and that a rather wide range of chain lengths is covered. All high polymers are

[1] TAMBLYN, J. W., R. W. MOREY, and R. H. WAGNER, *Ind. Eng. Chem.*, **38**, 473 (1945).

found to have more or less wide differential-distribution curves. In the case of natural high polymers, this distribution seems to be the consequence of a certain amount of degradation that takes place during the purification of the material in the manufacturing process. Figure 2 shows a few differential chain-length distribution curves of several high polymers.

These curves illustrate the fact that the average molecular weight or degree of polymerization does not give a complete picture. The amount of large and small chains may have an important effect on properties. The usual procedure is to obtain the distribution curve, compute the aver-
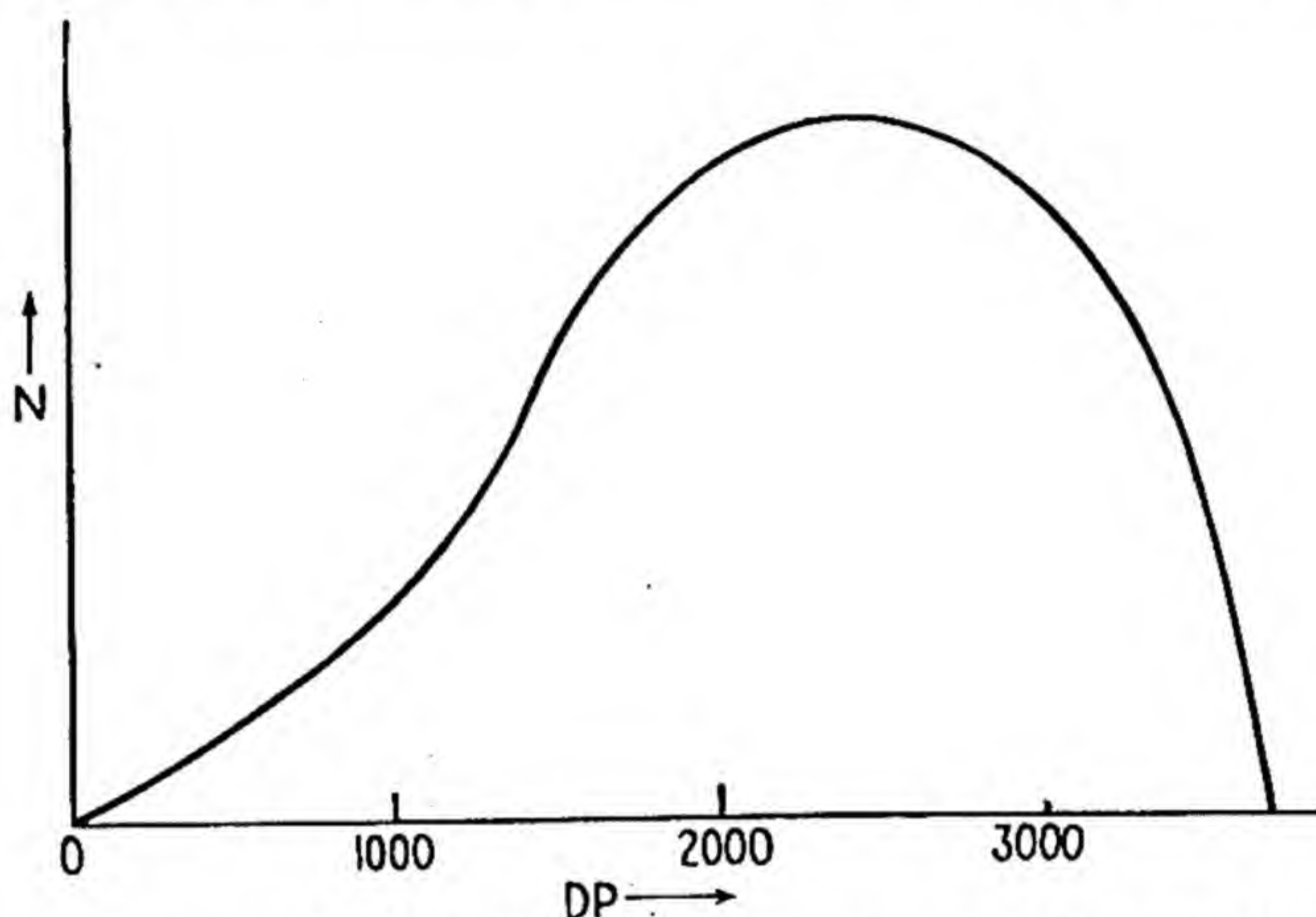

Fig. 1.—Typical differential distribution curve of number of molecules in the various degrees of polymerization.

age value, and use it as the average degree of polymerization of the material. In doing so, there are two different average values that can be obtained from distribution curves, the number-average degree of polymerization that is experimentally obtained by end-group titration and osmotic measurements, and the weight-average degree of polymerization that is the result of viscosity or sedimentation experiments. If a sample is very homogeneous, both averages converge to the same value; if the material has a wide distribution of different chain lengths, the weight average may be about twice the number average.

The average degree of polymerization and molecular weight distribution is greatly influenced by the conditions under which the polymerization is carried out. In general, it may be said that low temperatures and the absence of catalysts favor increase in molecular weight. However, in the manufacture of most commercial polymers, a compromise must be effected in order to obtain sufficient speed for economical operation. Also, the early stages of polymerization yield molecules of the highest molecular weight. Advantage is taken of this fact in many commercial operations

l y carrying the polymerization only partly to completion. Polymerization under isothermal conditions also leads to high average and uniform molecular weight distribution. In other words, it is important to avoid so-called "autopolymerization" under substantially adiabatic conditions which results in a polymer of poor tensile strength and that is brittle in character.

Mark[1] has summarized the effect of the degree of polymerization and the shape of the distribution curve on mechanical properties of linear polymers. In order to obtain any appreciable tensile strength, a polymer must have a degree of polymerization greater than a critical minimum
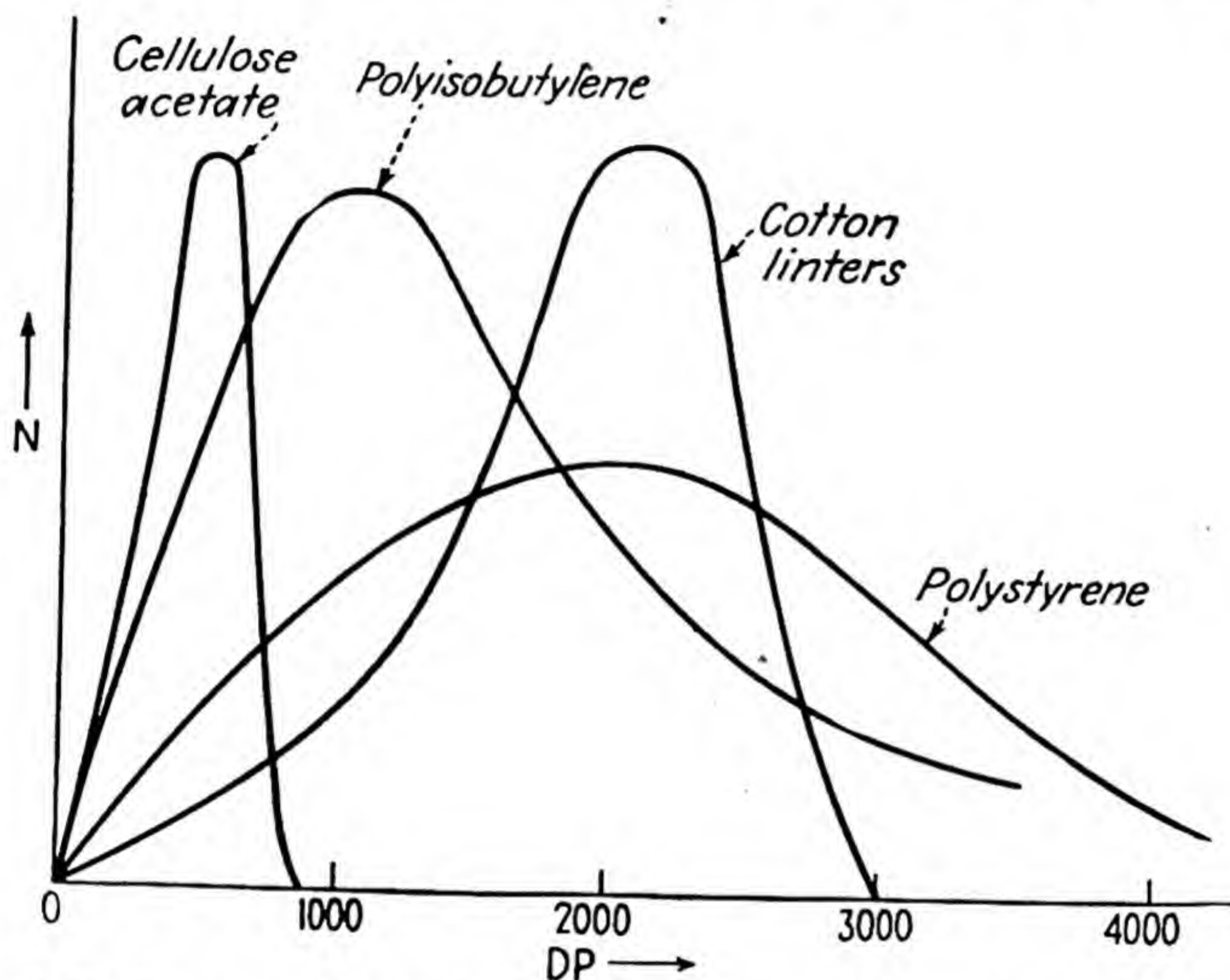
FIG. 2.—Distribution curves for various high polymers. [*Mark, H., Am. Scientist,* **31**, 104 (1943).]

value that usually lies between 40 and 80. The tensile strength in general increases with increases in the degree of polymerization until values in the neighborhood of 600 to 700 are reached. Above this value, the ultimate strength varies only slightly as the degree of polymerization increases. The actual shape of the distribution curve does not have as well a defined effect on the mechanical properties, although there is some indication that constituents of very low chain length are definitely detrimental.

The softening point of long-chain polymers is related to the magnitude of the forces tending to hold the chains together in the solid state. For a given molecular weight the flow point or softening point will be lower, in general, as the attraction between neighboring chains decreases. Cellulose exhibits marked attraction between chains and is closely packed, so that

[1] MARK, H., *Ind. Eng. Chem.,* **34,** 1343 (1942).

it should be very high melting.   Actually, it decomposes before softening appreciably.   Derivatives should show a decrease in softening point corresponding to a lesser attraction between chains and looser packing.   Cellulose itself cannot be made to flow by application of heat before decomposition is excessive, while solvent-soluble types of derivatives soften appreciably at moderate temperatures.   Both ethyl cellulose and benzyl cellulose show a decreasing softening point with increasing substitution, up to the point where maximum solubility occurs.   The softening point increases again until the hydroxyls have been completely replaced.   This maximum is far below the maximum for cellulose itself.

These physical properties are not entirely defined by the surface attraction between molecules, but are greatly affected by the average molecular weight of the chains.   Other factors being constant, the attractive forces between neighboring chains will be some function of the chain length. Increasing the degree of polymerization, and thus the chain length, of a given product tends to decrease the solubility and increase the melting or softening point.   The higher specific viscosity of the less soluble higher molecular-weight fractions of high polymers is usually quite apparent.

The shape of the molecule also has an effect on physical properties. Everything else being equal, irregular shapes cause a decrease in those physical properties which depend on the total force between chains or their arrangement.   This decrease can be illustrated by comparing derivatives of cellulose and starch, which has the same chemical composition as cellulose and is also a high polymer.   Starch differs primarily from cellulose in that it is a highly branched instead of a threadlike molecule.   This fact causes the tensile strength of films or threads of starch or its derivatives to be much lower[1] than is the case for the corresponding cellulose compounds.

Another type of treelike branching occurs in ethenic polymers.   If very highly branched chains are formed, they have a shape approaching that of a spherical or nearly spherical particle and differ from straight chains in their flow properties and in the distribution curve.   This type of branching is characterized by the fact that propagation and branching are going on simultaneously and differ greatly in degree, with a resulting wide variation in effect on tensile strength, softening point, etc.

Cross linking, on the other hand, is characterized by a structure in which there are comparatively short cross links between the chains.   The classical case of the effect of cross linkage is found in the vulcanization of rubber. The chains of rubber contain reactive methylene groups that add sulfur. The addition product is capable of reacting with reactive groups in other chains to produce sulfur bridges between chains.   As long as the cross bonds are not too frequent, of the order of one cross link on a hundred

[1] MARK, H., *Am. Scientist*, **31**, 110 (1943).

straight links corresponding to about 1 per cent sulfur by weight, the rubber retains its softness and flexibility and remains thermoplastic. This degree of cross linkage resembles the branched structures previously described as far as effect on some properties is concerned. If the cross bonds occur as frequently as 1 to each 10 monomeric units, the structure is very much stiffened and a hard thermosetting substance is obtained, which is insoluble, does not swell, and exhibits all the characteristics of a three-dimensional tight network.

Thus the effect of branching and cross linking eventually leads to a stiffening and increase in the hardness of the resin. Cross linking is particularly effective and leads to the thermosetting type of resin. Small amounts of branching apparently has little effect on mechanical properties but decreases solubility considerably and markedly increases temperature resistance.

Molecules of the solid polymer are held together by van der Waals' forces, which may approach primary valence forces, as, for example, in hydrogen bonding. As mentioned above, the forces between molecules will increase with the molecular size of the molecule, and in the case of linear molecules, they will be a function of the length. Because of the increase in attractive forces between molecules with increasing chain length, the dissolving of linear polymers will be more difficult than the solution of chemically similar smaller molecules. However, two other factors cause the force that is actually required to break apart two chains to differ from that which might be expected from the number of possible secondary bonds between chains. The first is the type of packing of the chains, and the second is the rigidity of the molecule.[1]

The type of packing determines the fraction of the theoretical maximum number of bonds that can exist between chains. Noncrystalline material, such as unoriented regenerated cellulose, is not regularly arranged and so has comparatively loose packing and few bonds between chains. For this reason it is more easily dissolved than a more crystalline material such as native cotton. In addition, the solvent can penetrate easily into such a material and can separate the chains at many points. Tightly packed material resists such penetration and must be dissolved gradually, beginning at the outer surface of the crystallite.

Two compounds having similar types of packing and the same type of attractive force between molecules may also vary in solubility owing to a difference in the rigidity of the chains. A very flexible high polymer can be dissolved by breaking each intermolecular secondary bond in turn, the equivalent of prying the molecules apart at one point. A completely rigid material cannot be as easily separated, since all the bonds joining one chain

[1] OTT, E., "The Chemistry of Large Molecules," Interscience Publishers, Inc., New York, 1943.

to the other must be broken simultaneously, in a manner resembling the pulling apart of two rigid bars that have been glued together.

Polyvinyl alcohol, starch, and cellulose are three compounds that illustrate marked differences in packing and rigidity. The intermolecular forces in polyvinyl alcohol and cellulose are approximately the same, and the packing can be made approximately the same. The polyvinyl alcohol, however, is very flexible and is water soluble. Cellulose, on the other hand, is one of the most rigid high polymers known and undergoes only a very limited swelling in water. Starch and cellulose approach each other in rigidity but vary in solubility because the differences in the shape of the molecules causes widely different packing.

The effect of the magnitude of the forces between chains of a high polymer is also important. This effect may be more responsible for the solubility behavior than any other factor. The extremes of intermolecular forces may be illustrated by comparing a linear polymer that is very loosely held together in the solid state with a material in which a considerable number of cross links have been established by chemical bonds. Crude rubber and hard rubber are examples of these extremes.

EFFECT OF PLASTICIZERS ON LINEAR POLYMERS

High polymers show maximum freedom of motion of sections of the chain in solution, and the nearer the approach to solution, the greater the flexibility. This is actually what occurs in the solvent type of plasticization. Powerful solvents of low volatility are employed to push the chains apart, causing irregularities in the arrangement of the chains with respect to one another and lowering the attraction between chains. This permits more freedom of movement between the chains with consequent improvement of flexibility.

Solvent-type plasticizers vary to a considerable extent in their effect, depending on their affinity for groups present on the chains and on the size of the plasticizer molecule. Camphor in nitrocellulose forms an ideal plasticized system in that the nitrate group of the cellulose and the keto group of camphor unite with the formation of a double compound, and the rigid shape of the camphor molecule enforces a high degree of separation between chains. The degree of flexibility can be varied in a given system by the amount of the plasticizer used. As more and more plasticizer is employed, increasing separation of the chains results, and the behavior of normal solutions is more and more closely approached. The plasticizing group or groups may be permanently combined with the chain in the form of a stable derivative, but the effect on flexibility will be much the same. Such products can be considered as being internally plasticized. The vinyl chloride–vinyl acetate copolymer is an example of this type. There is

another type of plasticization known involving gel formation which has a similar resultant increase in flexibility. Whatever factors lead to increased solubility also lead to increased flexibility, as would be expected in view of the freeing of the linear polymer molecules from the influence of their neighbors.

Plasticizers may be active solvents at elevated temperatures, at room temperatures, or over the entire range. Nonsolvent-type plasticizers are also used which, in general, reduce flexibility and extensibility but maintain the tensile strength and resistance to abrasion.

The permanence of the physical properties of plasticized products upon aging depends to a large degree on the retention of the plasticizer. The physical properties of the plasticizer, such as melting point, vapor pressure, specific gravity, surface tension, and viscosity, are useful in predicting their behavior.

Another important property of the plasticizer is the acidity or tendency toward hydrolysis. Moisture susceptibility depends to a considerable extent on this property.

Plasticizers are often added to increase resistance of the product to special conditions. For example, the triphenyl and tricresyl phosphates are useful to retard burning rate.

The amount of plasticizer required to give desired softening point and flow, together with flexibility, tensile strength, and impact strength, in the molded plastic is very important. In general, the smaller amount of plasticizer required to give the desired combination of properties, the better the plastic. Broadly speaking, the use of a plasticizer is a compromise used to make up for the deficiencies in the polymer, and the ideal plastic should require no plasticizer.

PART II

GENERAL APPLICATIONS OF RESINS

Resins are used for an almost infinite number and variety of purposes, and new applications are constantly appearing. Gradually, over a period of several decades, they have become a material of construction just as glass and ceramic ware are materials of construction. In the forming of relatively small objects, they rival the metals in variety and number of applications. Synthetic fibers made from resins are an appreciable percentage of the total fiber production, and the use of resins in coatings has reached a considerable tonnage. If we add such applications as adhesives, impregnating agents, and modifying agents, which, although of lesser importance from the standpoint of tonnage, cover a large and varied field, a broad picture of the scope of applications of resins can be obtained. No other class of materials is applied in such a variety of ways or has such widely divergent end uses.

However, many end uses depend on the final mechanical alterations of an intermediate plastic form, just as a great variety of objects can be obtained by mechanical operations on standard stock metal shapes. Many resins are almost as readily machinable as metals, so that metal-forming operations such as cutting, drilling, and tapping are common in the production of finished plastic articles. Methods of joining utilizing adhesive bonding are almost as common as the analogous welding operation in the field of metals, and forming operations such as molding and extrusion are always associated with the uses of resins and plastics. Since forming methods are not confined to rigid solids and liquid melts but can be extended to solutions and nonrigid fluids or rubbery materials, the variety of forming methods is even greater than with metals.

The numerous varied and complicated combinations of methods employed to produce all types of plastic products can be greatly simplified if final forming and finishing operations are not considered. In a similar manner, the description of the production and uses of standard steel shapes is a simple matter compared with a discussion of the methods of fabrication and uses of all steel articles that might be made from standard shapes.

If the final finishing operations and mechanical alterations by machining, etc., are not considered, there are six general classes of applications of resins; these applications will be discussed later in more detail.

1. *Coatings.*—The use of resins in coatings extends from protective coatings, such as varnishes, to coated fabrics and papers. They are applied

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for purposes of surface protection, decoration and, in general, to alter the physical properties of the surface.

2. *Molded and Cast Articles.*—This application is generally thought of when the term "plastics" is mentioned. It involves the production of relatively small objects, in which the final form of the finished article is approximated by a molding or casting process. Normally, only finishing operations are required to produce the finished article. A tremendous variety of products are produced by these methods, extending all the way from buttons to radio cabinets.

3. *Standard Shapes.*—The production of standard shapes is analogous to the production of structural shapes in the steel industry. They are produced by molding, laminating, casting, and extrusion and take the form of sheets, rods, tubes, and special profiles. Since molding, casting, and laminating methods are employed, the actual processes are similar and, in some cases, identical with those employed to produce molded and cast articles. However, their use usually depends on additional machining or fabricating methods to produce a finished product.

4. *Adhesives.*—Resin adhesives are becoming increasingly important and their applications more and more varied. The actual tonnage of resins used in the production of adhesives is small in comparison with other applications, but their importance in the fabrication of a great variety of products is such as to warrant their consideration as a special application of resins.

5. *Fibers, Filaments, and Foils.*—These products are all produced by extrusion methods, but differ from other applications of the extrusion process in that small diameters or relatively thin sections are produced. Large tonnages of resins are used for this purpose, approximately equaling the entire resin production for other purposes if rubber and the synthetic rubbers are excluded. Their importance in the production of textiles and in packaging is, and has been, increasing at a remarkable rate.

6. *Impregnating Agents.*—Resins are used to impregnate a variety of porous materials. This application is not new, but it is only fairly recently that resins and methods have been developed that completely alter the physical characteristics of wood and textiles to permit much wider applications of such materials and much more satisfactory service from them.

It should be realized that there are other applications of resins which do not come under these six main headings. These applications are usually of minor importance from the standpoint of tonnages involved but may play an extremely important part in an industrial process. The use of resins in the softening and purification of water is a good example. Such applications will be taken up under the discussion of the particular resins that are used for such special purposes.

COATINGS

The most common use for resins in coatings is in varnishes, enamels, and lacquers of various types. Varnishes are ordinarily of two main types: the oleoresinous varnishes, in which resins are dissolved in an oil such as linseed oil; and the "spirit" varnishes, in which resins are dissolved in volatile solvents such as alcohol or low-boiling esters. In the first type, the coating is produced by oxidation, condensation, and polymerization. Spirit varnishes, however, form a coating from the resin that remains after the solvents evaporate. This is also the manner in which coatings are formed by lacquers, except that the term "lacquer" is ordinarily reserved for solutions of cellulose derivatives such as the nitrate and acetate. If pigments are ground into a varnish, an enamel is produced. If the proportion of resins to oil is relatively small, gloss paints result.

There are a great variety of varnishes, varying all the way from the ordinary type of wood finishes to printing inks. Most of the commercial resins are used in coating agents of various types. In many cases, a blend of two or more resins may be used to produce the desired product. A great variety of other materials may be added to modify or enhance the properties of the varnish. Pigments, fillers, and plasticizers are most commonly encountered, but everything from a catalyst to sand may be added for special purposes. The various specific uses of the different resins in coatings will be discussed in more detail under the particular resin involved.

Coatings are applied by spraying, brushing, dipping, slushing, knifing, rolling, printing, and calendering. The first two methods are generally used for surface finishes on wood or metal but may also be used for other special applications. Dipping and rolling are extremely important operations in the coating of fabrics and papers (see Fig. 3). The coating is usually applied continuously by running continuous sheets through vats containing the coating agent or to application rolls that roll it over the surface. Knifing is also used to spread coatings on fabrics or papers. The knife spreader is a relatively simple apparatus in which a knife blade spreads out a pool of resin mixture or varnish over the entire surface of a moving belt of fabric or paper. The varnish is applied by running a small stream on the fabric just ahead of the knife. It is most suited to the application of light coatings; although by the use of a multiplicity of light coats, the heavy smooth films necessary in artificial leather manufacture are laid down. It is not uncommon to use as many as 20 passes through a machine to build up the desired film thickness.

Calendering permits the application of a smooth heavy film up to a thickness of two or more thousandths of an inch. The coating mixture is prepared by working the resin, plasticizer, and modifiers together on a heated two-roll rubber mill. When sufficiently milled, the mass is stripped

from the rolls in sheets and kept until needed. Then the sheets are again put in the heated mill and brought to a proper temperature, which varies with the type of plastic used and the surface to which it is applied, whereupon the mass is fed to the top rolls of the calender. In the case of a three-roll calender, the top and middle rolls meter the mass and squeeze it to a uniform and predetermined thickness over the middle roll. The film is then brought in contact with the cloth passing between the middle and bottom rolls, and it adheres to the material being coated in preference to the heated middle roll. The coating calender is usually run slower than
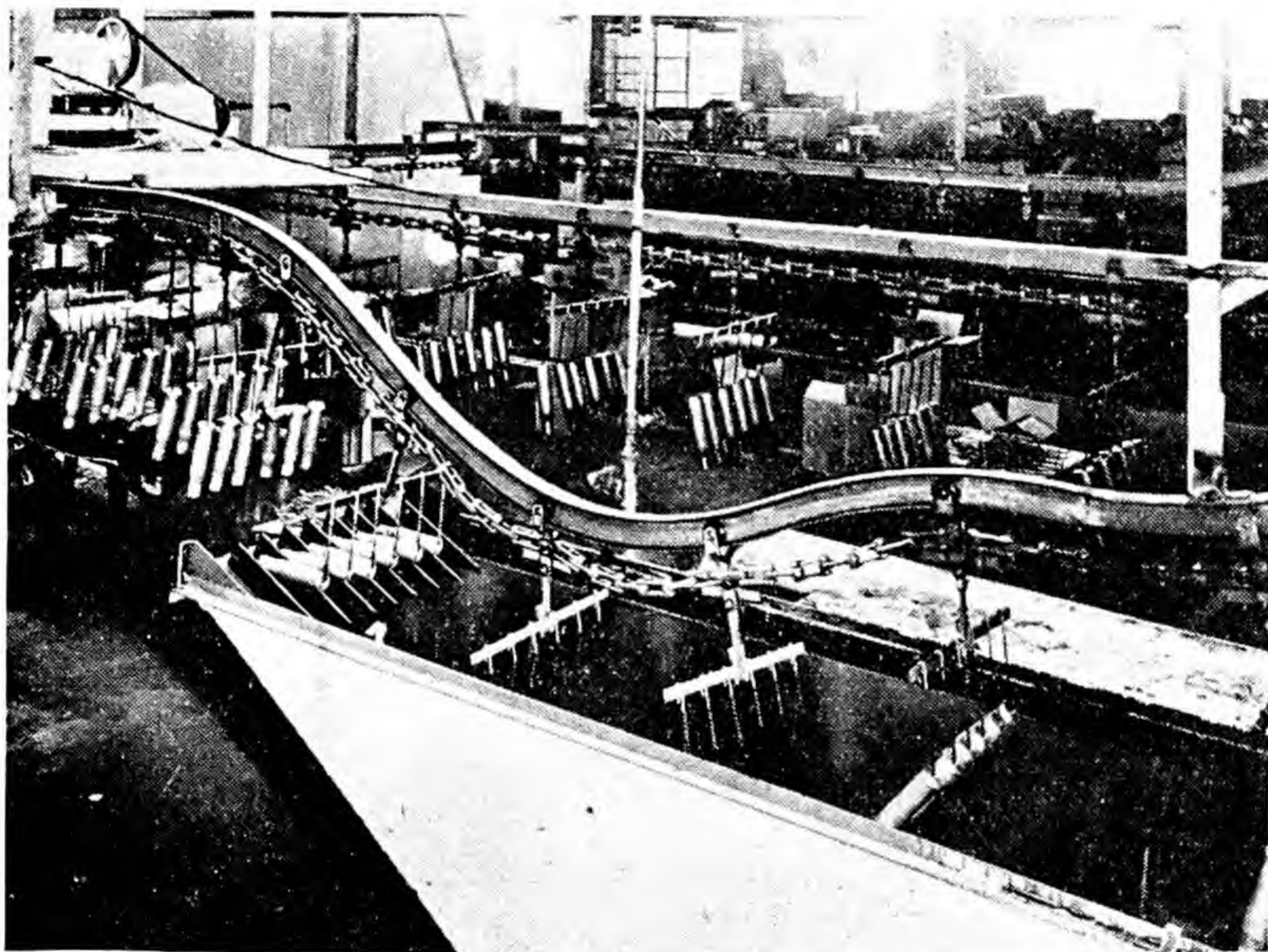
Fig. 3.—Continuous dip coating of small objects. (*Bakelite Corp.*)

the knife or roll machine; but since only one coat may be required, the total coating time is less for everything but a very thin film.

Slush coating is the only practical method of coating the insides of containers that are too small for the use of spray equipment. The operation consists of partly filling the container, closing all openings, and then tipping and rotating until the inside surface is completely coated. The container is then carefully drained and the coating dried or baked.

Coatings may be applied to produce a finished surface, as is true of the common usage of paints and varnishes, or they may be applied for further processing as in the production of laminated materials. In the production of laminated shapes, the coating, of course, also serves as an adhesive and, in the case of porous materials, actually impregnates into the material. In this respect, adhesives and impregnating agents are special types of

coatings, but since their function is that of welding rather than the modification of a surface, they should be considered separately. The printing process is used for the application of printing inks and special designs that may be applied by printing.

A special method of spray coating is the Schori flame-spraying process (see Fig. 4). In this process, finely divided resin powders are blown out of a special burner nozzle by means of compressed air or oxygen. Acetylene or other gases are used to produce the flame. The powder is dispersed
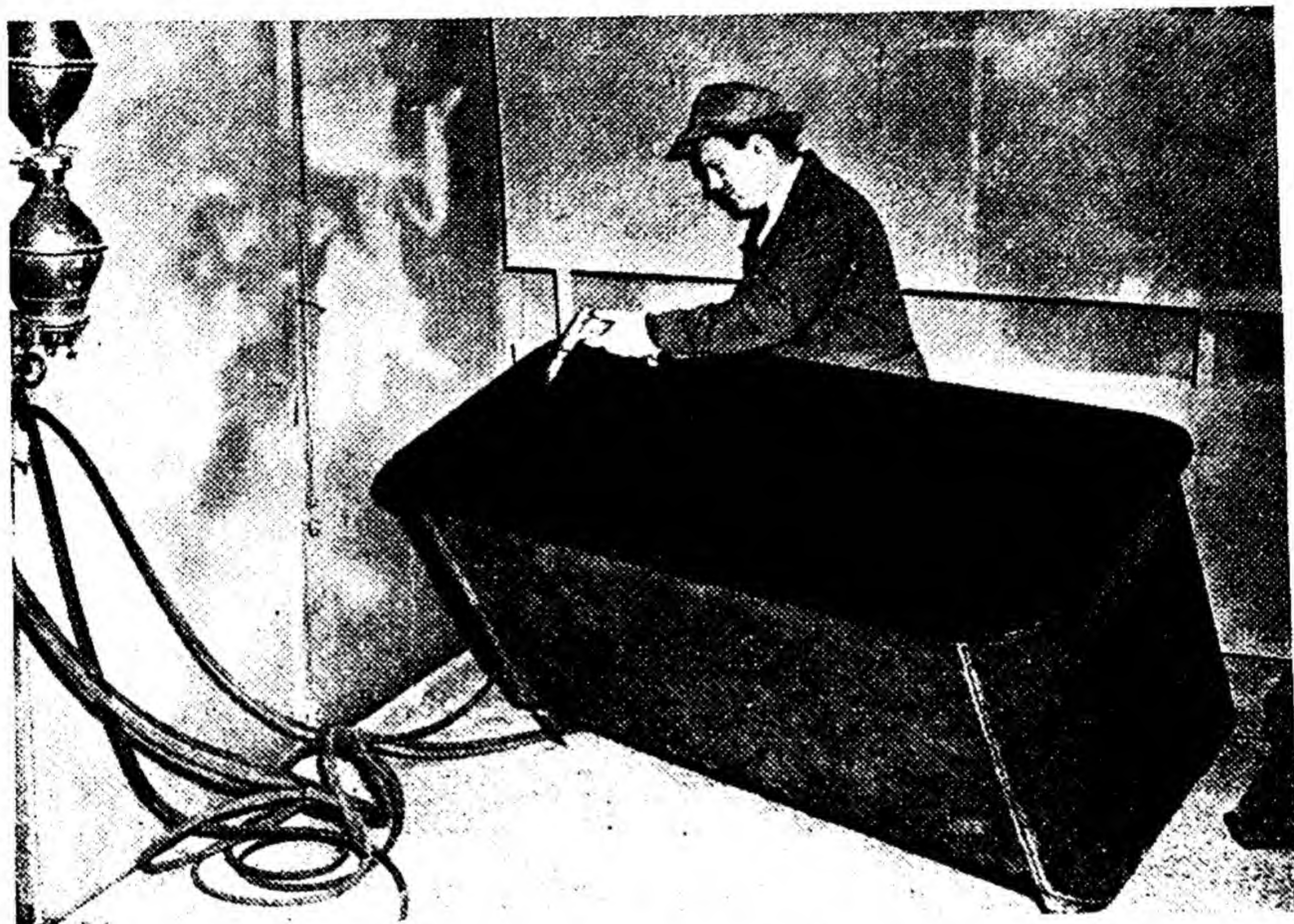
FIG. 4.—Coating the inside of a tank by the flame-spraying process.   (*Schori Process Corp.*)

through the flame and onto the surface to be covered. The high temperature of the flame and the large surface area of the particles cause them to soften and adhere to form a continuous coating that has excellent adherence. Electrically heated nozzles have also been developed that form the coating in a similar manner. Since no solvents are used in this process, drying time is greatly reduced, with a corresponding decrease in the cost of operation.

All other coatings must be dried to form and harden the film. A great variety of drying methods are used, from simple air drying at room temperature to rapid baking at high temperatures. Usually the variation in drying procedure depends primarily on the various methods of applying heat, but the means by which volatile solvents are removed also produces differences in methods. Some resins require the elevated temperatures obtained by baking before they will undergo the final polymerization that

produces a hard, durable film. These "baking" enamels produce the most wear-resistant, hardest films but are limited to objects that can be heated to the relatively high temperatures required.

A special type of coating has been developed in which the varnish or enamel is emulsified in water. This combines the advantages of an oil varnish with the greater fluidity and ease of application of a solvent-type coating. In addition, it permits coating a damp or wet surface without
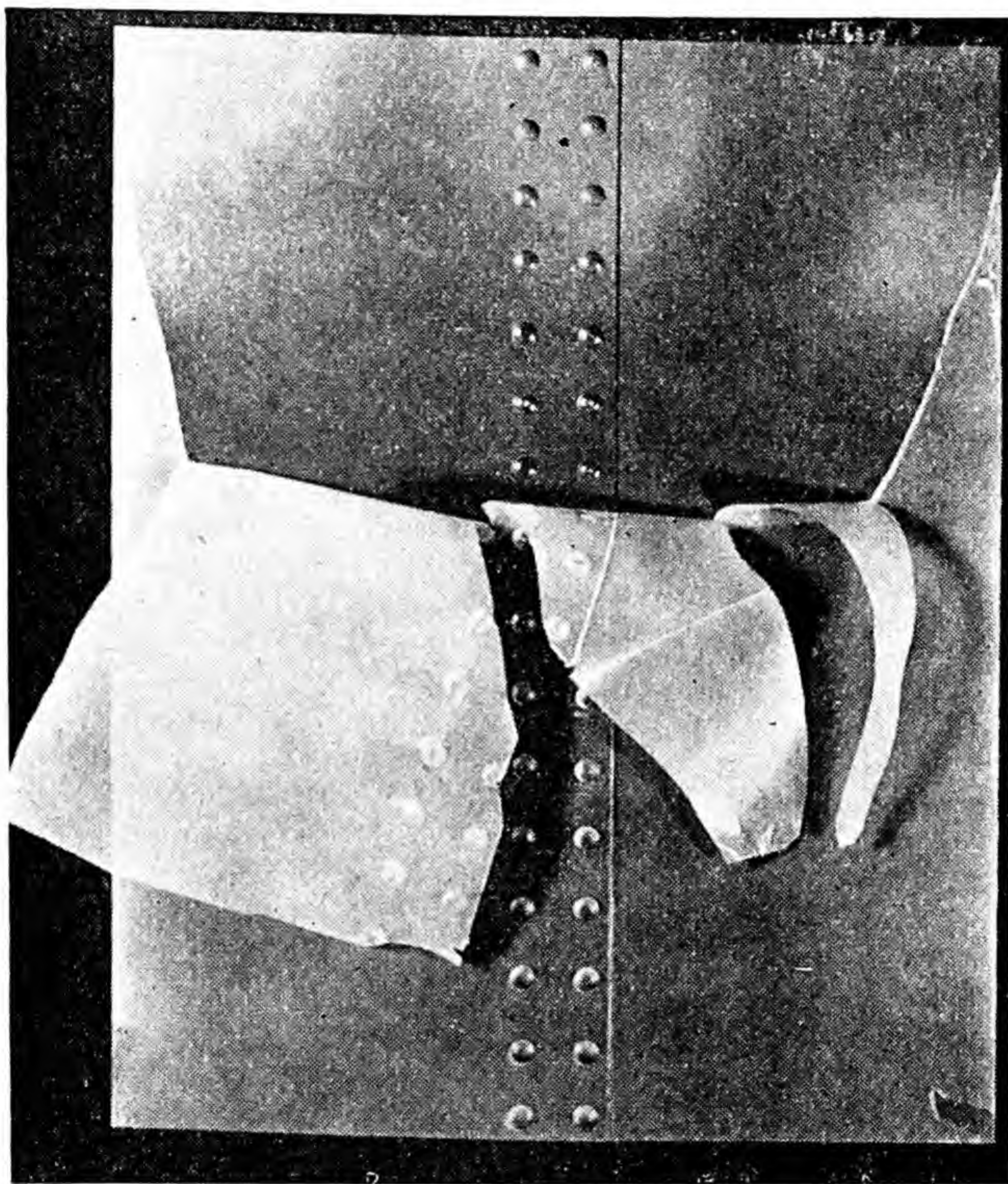

Fig. 5.—Removal of protective strip coating. (*Bakelite Corp.*)

danger of poor adhesion. The coatings formed by this method are particularly resistant to water and washing. Formulation of coatings by this method has opened an entirely new field, and many developments and special applications can be expected.

Temporary coatings have become extremely important in the last few years as a means of protecting surfaces during shipping or handling. Special problems are involved in that they must be easy to remove (see Fig. 5). Special uses vary all the way from the protection of machined or polished surfaces of metal parts until they are ready for assembling to the complete film coating of metal airplanes for ocean transportation and the

protection of guns for storage (see Fig. 6). The coating is of a composition that will peel or strip readily once a break is made (see Fig. 5) but is imp˻·vious to moisture or corrosive conditions as long as the film is unbroken. An analogous application is involved in the plastic seal placed over bottle closures by the dipping process.

Fig. 6.—Protective film coatings for storage of ordnance.

MOLDING AND CASTING

Molding is defined, "to form in or into a particular shape." This simple definition, however, does not indicate the tremendous variety of applications of the molding process even exclusive of extrusion, which will be discussed under the production of standard shapes.

Plastic molding materials are divided into two main classes: thermosetting or hot-set plastics and thermoplastic or cold-set plastics. Thermosetting resins not only require heat for plasticization, but also the application of proper heat for a period of time to polymerize or set them. These materials are usually molded by the compression process, where the material is loaded directly into the mold cavity, or by transfer molding, where the molding powder is plasticized by heat in an external chamber and then quickly transferred to a hot mold where it is set or hardened.

Thermoplastic materials require heat to plasticize them, but they must be cooled to harden and retain their shape. This requires a cyclic process of temperature control for compression molding in which the mold is first heated and then cooled before the ejection of the finished article. Injection

molding of thermoplastics is similar to transfer molding in that the material is plasticized in an external chamber, but it is injected into a cold, rather than a hot, mold.

Molds can be divided into five main types: (1) positive mold, (2) flash mold, (3) semipositive mold, (4) injection mold, (5) transfer mold.

The positive-type mold (see Fig. 7) is desirable where the casting must be very dense, since all the molding pressure is applied to the projected area of the molded piece. It is also used for molding high-impact plastics.
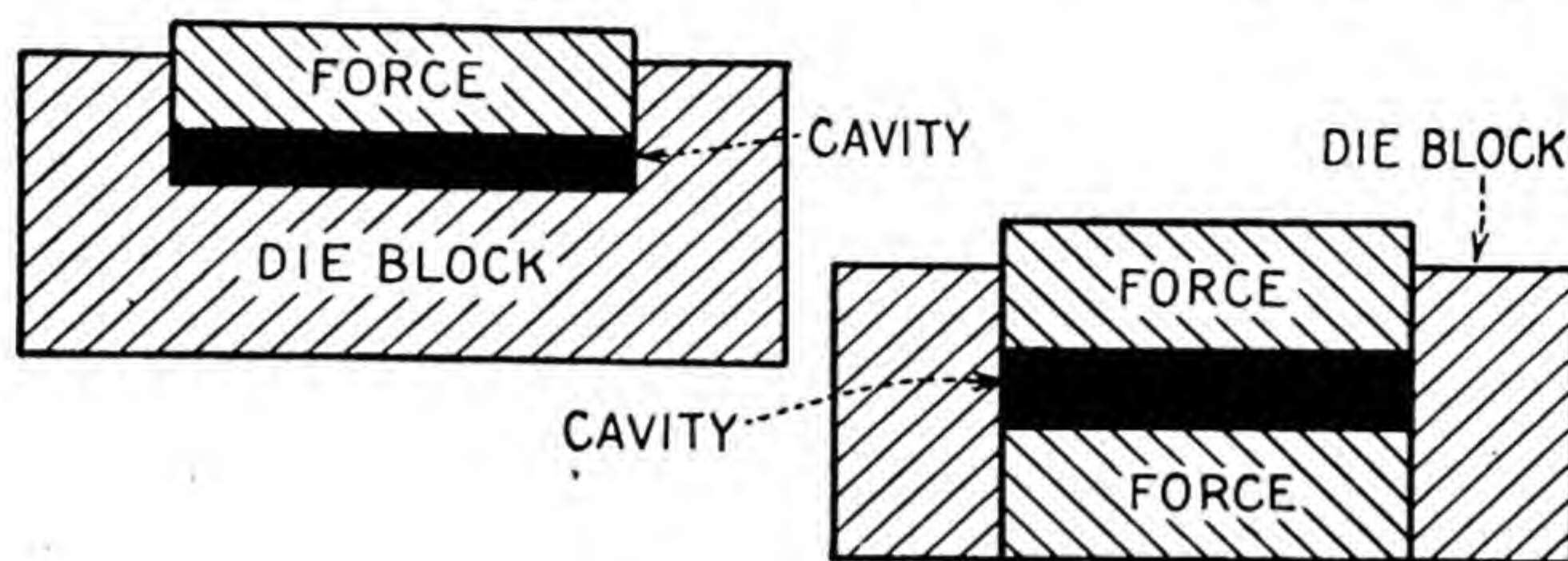
FIG. 7.—Positive mold.

A landed positive mold is generally used where it is necessary to split the mold horizontally to accommodate a radius, bevel, or some necessary projection. Provided that a tight fit between force and cavity is maintained, the positive mold ensures full pressure on the compound. There
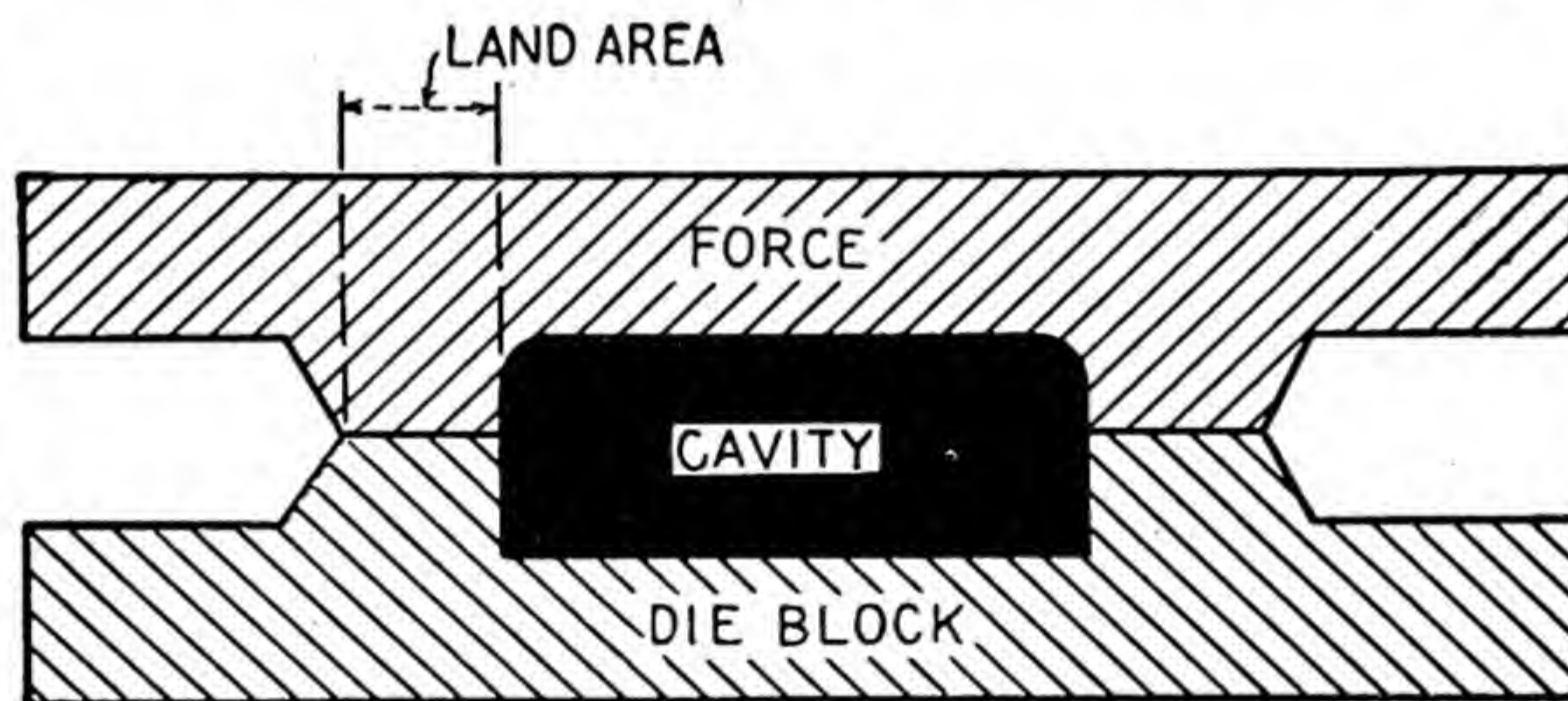
FIG. 8.—Flash mold.

is then little or no overflow, and effective pressure is maintained. When the fit between force and cavity of a positive mold is made loose to allow overflow, or sprue grooves are added and external press stops are employed to determine the depth of cavity, maintenance of pressure on a compound becomes impossible.

The flash-type mold (see Fig. 8) is generally used in producing thin pieces and where a preform is used for the charge. This type of mold is probably the least expensive. There must be relief around the cavity either on the lower or upper part of the mold or sometimes on both, so that there is only a comparatively small area, called the "cutoff," in contact when the mold is completely closed.

As molded items have increased in size and complexity, and the depth of draw has measurably increased, it has become desirable to resort to a combination of the positive and flash-type mold, now commonly referred to as "semipositive" mold (see Fig. 9). The use of such a mold produces a piece having a maximum density, inasmuch as the material is under pressure during its plastic stage and for some few seconds after the mold
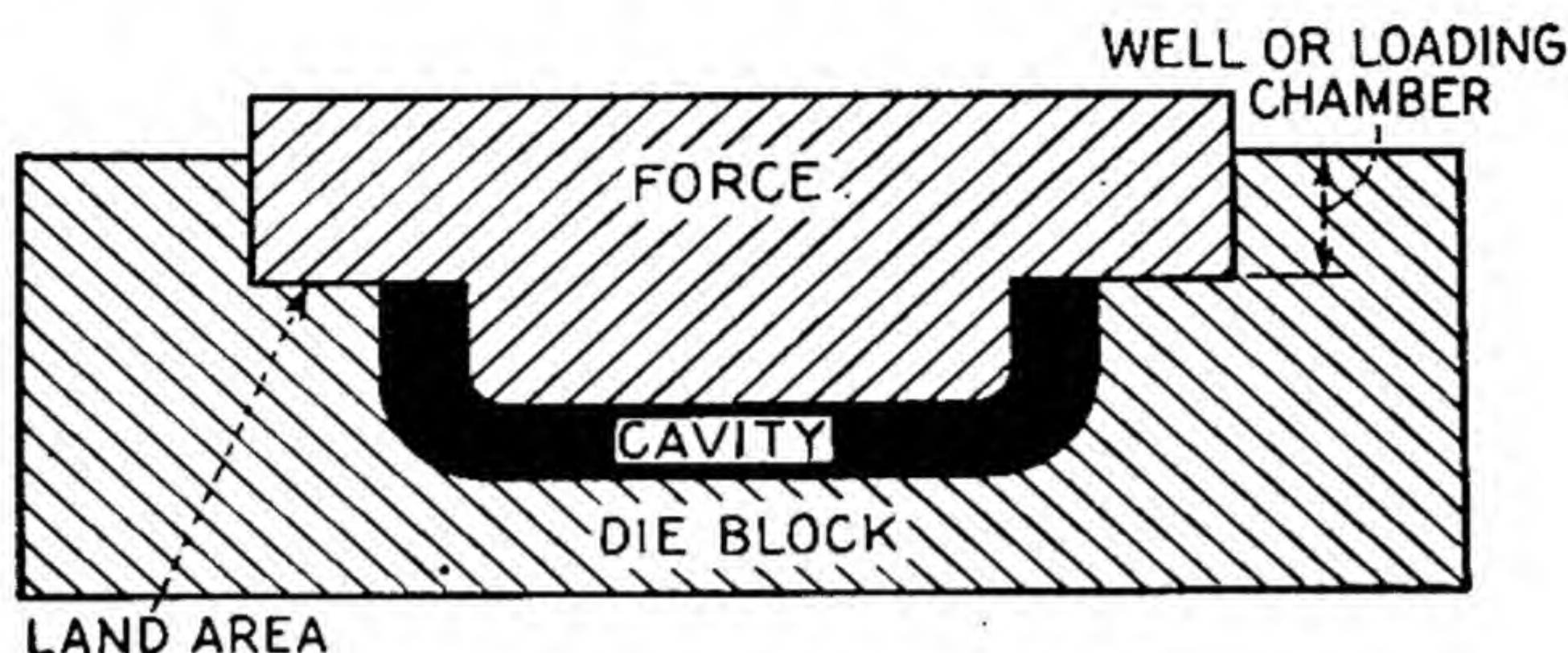

FIG. 9.—Semipositive mold.

has seated on the cutoff edge. The term "semipositive" is applied rather loosely in the molding field, and many so-called semipositive molds are really flash molds.

Transfer and injection molds differ from the previous type in that they are closed when the actual molding operation takes place. A transfer mold is shown in Fig. 17 and an injection mold in Fig. 14. The operation of these molds resembles casting.

MOLDING PROCESSES

There are several methods of molding: (1) compression molding, (2) injection molding, (3) transfer molding, (4) jet molding, (5) postforming, (6) low-pressure molding, (7) blow molding, (8) casting.

Compression Molding.—Compression molding is the technique applied to the process of flowing plastic materials into mold areas by the pressure caused by the compression of molding powder between two parts of a hot mold. It is by far the most widely used method of molding. The mold is heated, preferably by steam, and a measured charge of molding compound is put into the lower half of the mold (cavity). This charge may be a weighed amount of material, a predetermined size pill, or a volumetric amount. The mold is then slowly closed until the material starts to flow, at which time the rate of closing of the mold is slowed down to an almost imperceptible speed. After the excess material has flashed out and the upper part of the mold has seated on the cutoff areas of the cavity, the mold is allowed to remain closed for a definite period of time to cure the resin if a thermosetting material is being employed. The length of cure is

dependent upon a variety of factors, such as the speed of cure of the molding compound, thickness of the molded piece, over-all size of the piece, and temperature of the mold. If thermoplastic resins are being molded, the mold must be cooled with cooling water. After the mold has been closed for the requisite period of time, it is opened and finishing operations such as definning, buffing, and inspection take place.

A great deal of careful engineering must precede the relatively simple operation just described. The proposed piece must be properly designed, including freedom from undercut, sufficient draft on side walls, proper consideration of bosses, and other similar constructional features. Some materials work better in one type of mold, others in another. The resin must have the proper plasticity depending on the size of the molded piece and the pressure available.

In compression molding the correct amount of molding compound must be used. Too little results in pieces with unfilled areas. Too much is wasteful and requires added pressure. Usually 3 to 10 per cent excess material is required over and above that in the finished piece. It is better in molding small objects such as buttons and wall plates to use pills of proper weight. Where this is not feasible, loading boards or cups are required. Inaccurate methods of loading invariably increase production costs.

Theromosetting compounds must be left in the mold long enough to cure. It is ususally necessary to have adequate timing devices to aid the operator in maintaining the proper cycle. Many molders are attaching automatic press-operating devices to their equipment, and fully automatic presses are available.

Most presses are hydraulically operated. The hydraulic system may consist of self-contained units or may be connected to an accumulative pressure system (see Fig. 10). Water or oil is used to convey the pressure to the working parts. With any given line pressure, any reasonable number of presses may be operated, the pressure available at any press being controlled by the area of its ram.

The upstroke press is the commonest. Here the hydraulic ram and cylinder are mounted on the floor and the upper platen remains fixed, the lower platen traveling up to close the press. With this type of press it is common to use auxiliary cylinders and rams, known as "pullbacks," to open the press. The down stroke press differs from the upstroke press in that the bottom platen remains stationary while the upper one moves.

The angle press, frequently called the "side-angle press," was developed to allow pressure to be applied to the mold in a perpendicular direction, allowing for commercial consideration of split molds. Such molds are required for certain designs involving undercut, external threaded parts, and the like.

Preforming.— Preforming consists of shaping the various types of molding powders into tablets or pills of definite weight. This is accomplished by two types of machines especially built for such an operation. Both utilize the same principle, but the size and volume of production are different.
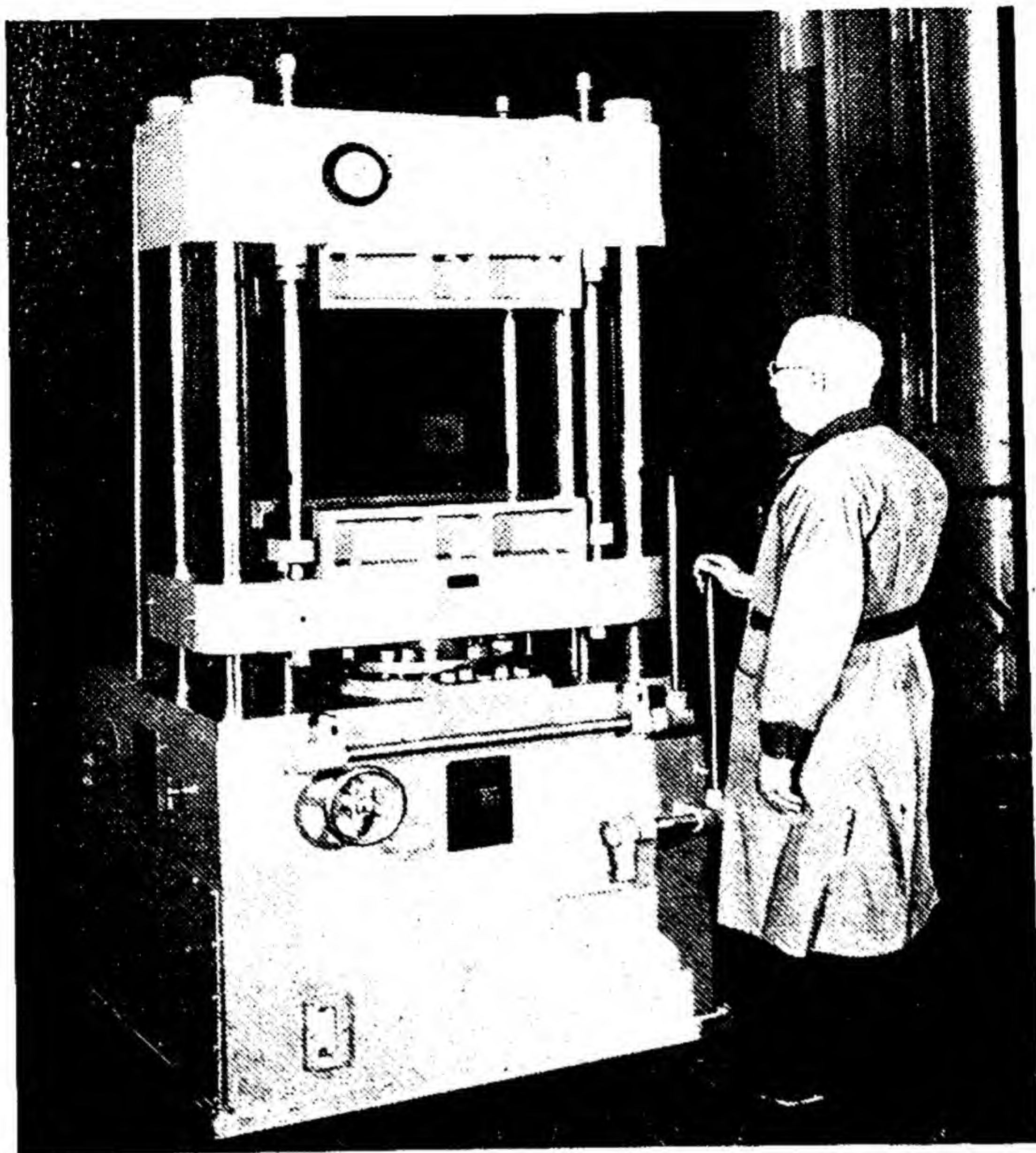

FIG. 10.—Semiautomatic hydraulic press for compression or transfer molding. (*The Hydraulic Press Manufacturing Co.*)

The single-stroke machine accomplishes preforming by a vertical piston-like movement. The preform die cavity is stationary and is fed automatically after each stroke by a shaker arm connected to the material feed hopper. The advantage in this type machine lies in the fact that odd shapes and sizes can be produced easily and that only one die is needed. The production of the machine varies with the size of the preform but usually runs between 35 and 70 strokes per minute.

The rotary preformer (see Fig. 11) represents high-speed production. By means of moving parts and continuous feed, between 200 and 800 pills per minute are possible. The ordinary rotor has 23 stations or places where a pill is made. This means 23 dies and punches.

Injection Molding.—The process of injection molding consists essentially of transforming granular thermoplastic material into a flowing state by the application of heat and by forcing it under high pressure, usually averaging 20,000 to 35,000 lb. per sq. in., into a cool mold, where it hardens. In actual practice the process is almost entirely automatic. The operator's
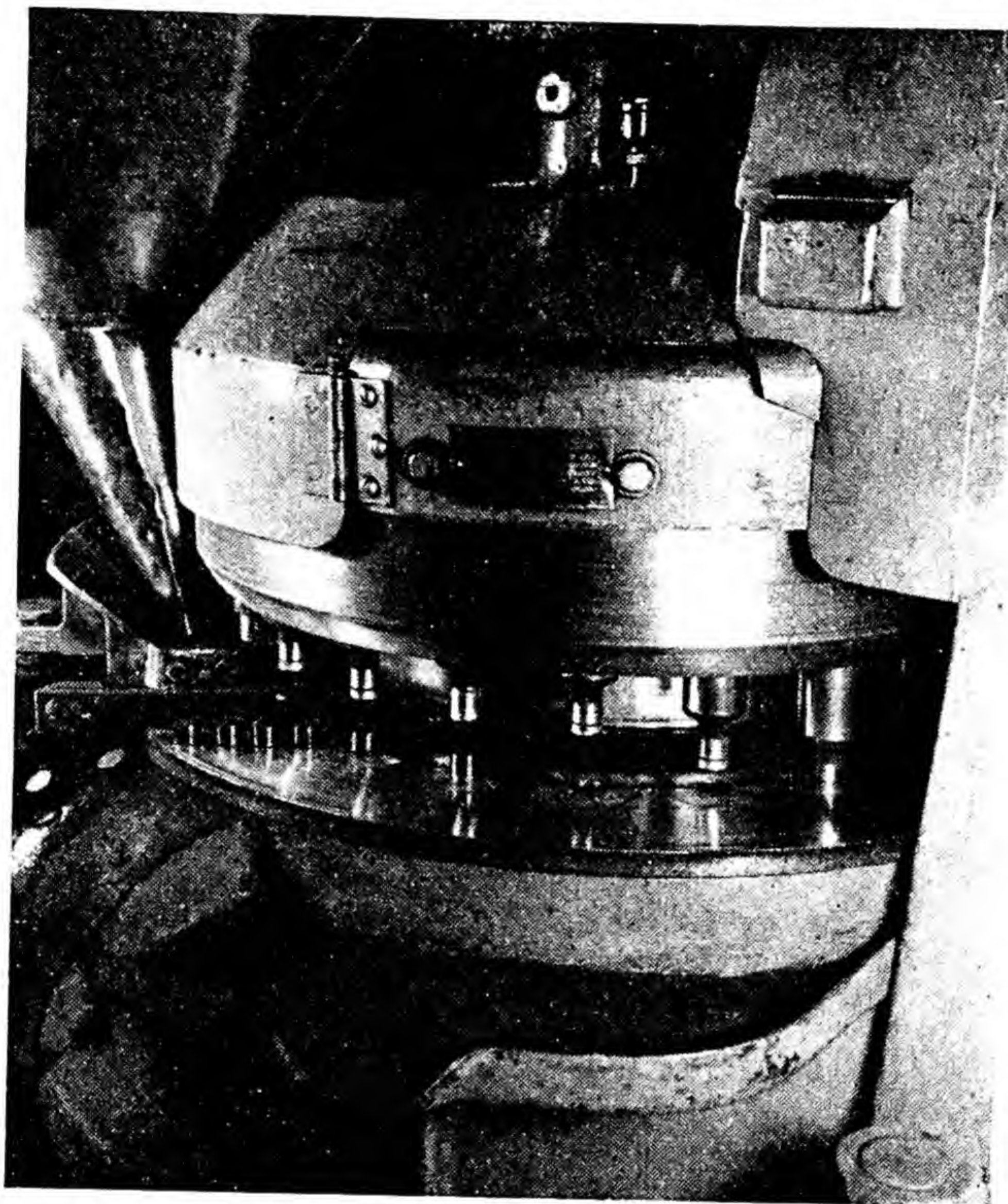

FIG. 11.—Rotary preforming machine. (*Bakelite Corp.*)

duties consist mainly of closing the mold by means of electrical controls. Ejection of the finished article from the molds may or may not be automatic.

The operation of all standard commercial injection-molded presses is similar (see Fig. 12). The plastic material is placed in a hopper from which it is fed in a predetermined quantity to a heated chamber located in front of a hydraulically actuated piston. After the mold is closed, the piston forces the plastic through an electrically heated cylinder around a "torpedo" and then through a nozzle where it is pressed through the sprue opening in the front half of the die. The plastic then flows through runners in the die into the cavities. The pressure holding the die closed and that used to inject the plastic material are applied until the molded article is ejected either automatically or manually (see Fig. 13). While the cooling cycle
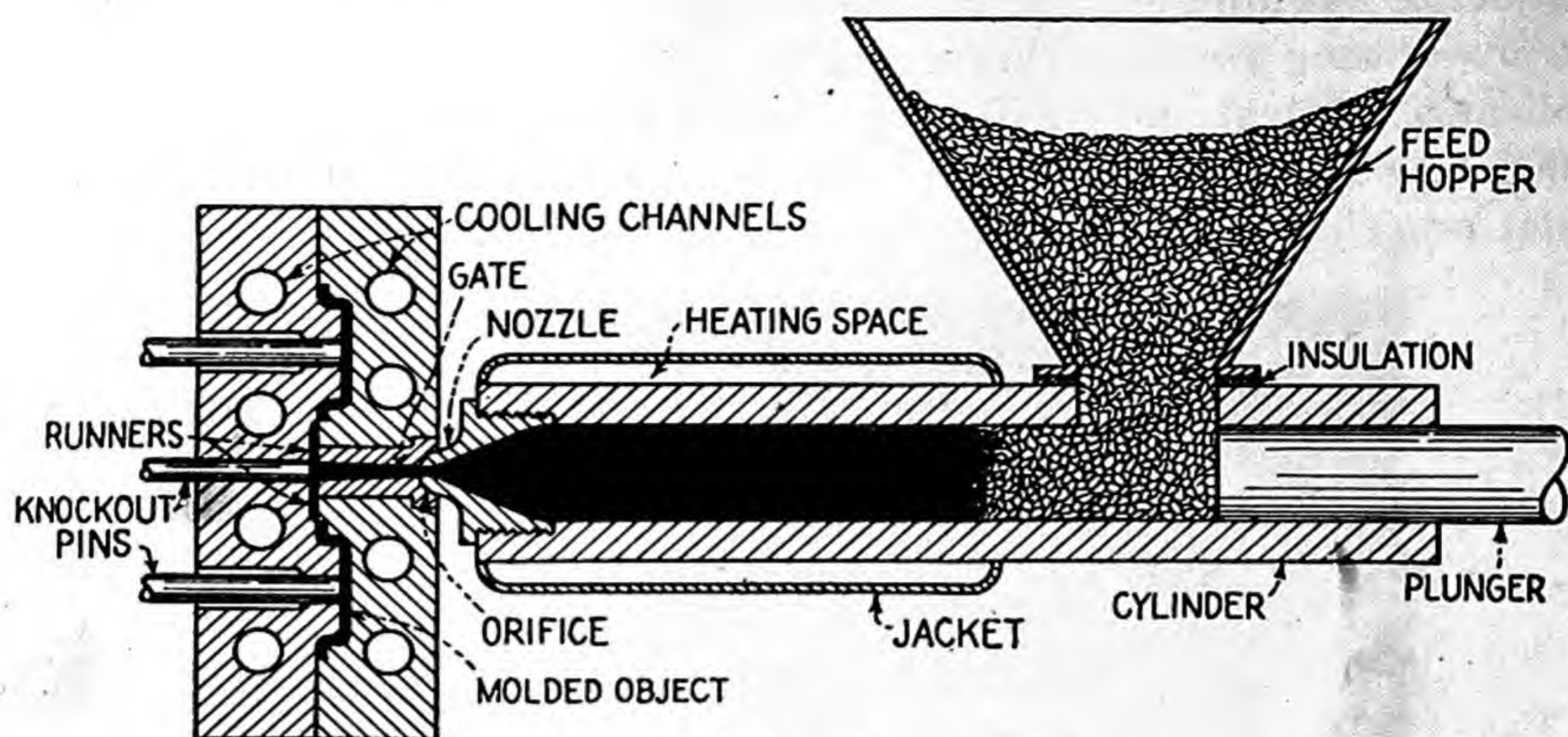
FIG. 12.—Diagram of an injection-molding press. (*Tennessee Eastman Corp.*)
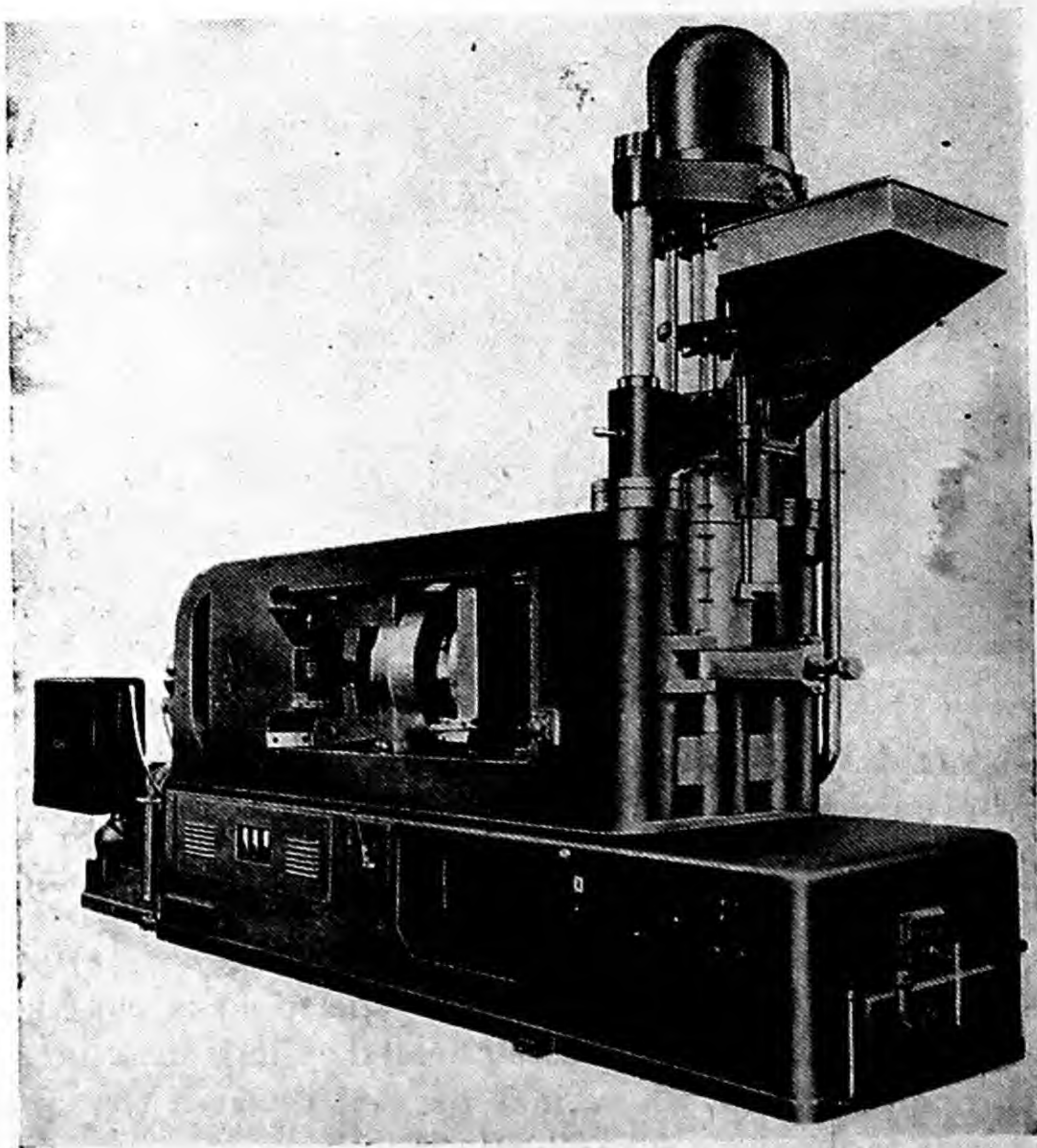

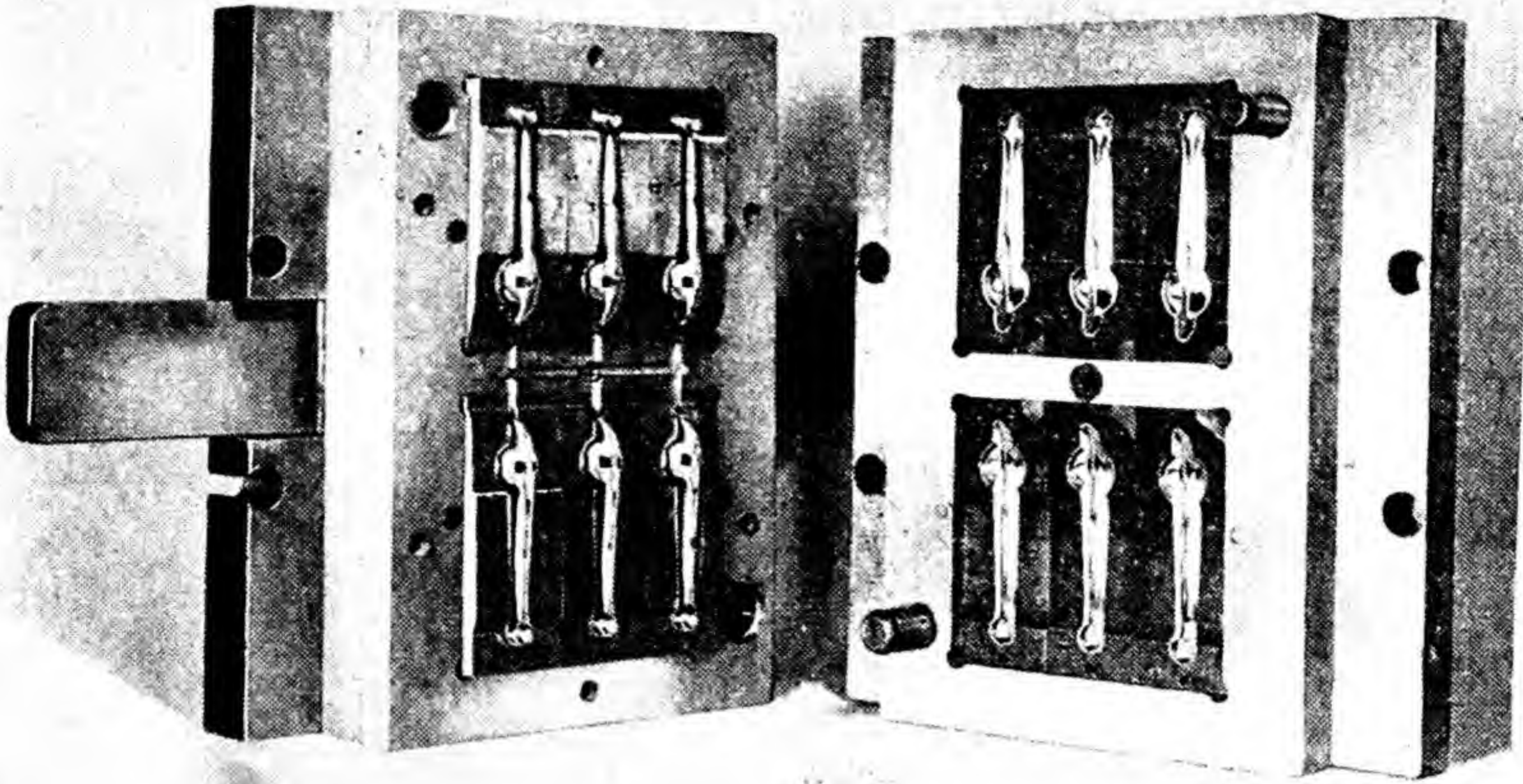FIG. 13.—Injection press with vertical plunger. (*Lester-Phoenix, Inc.*)

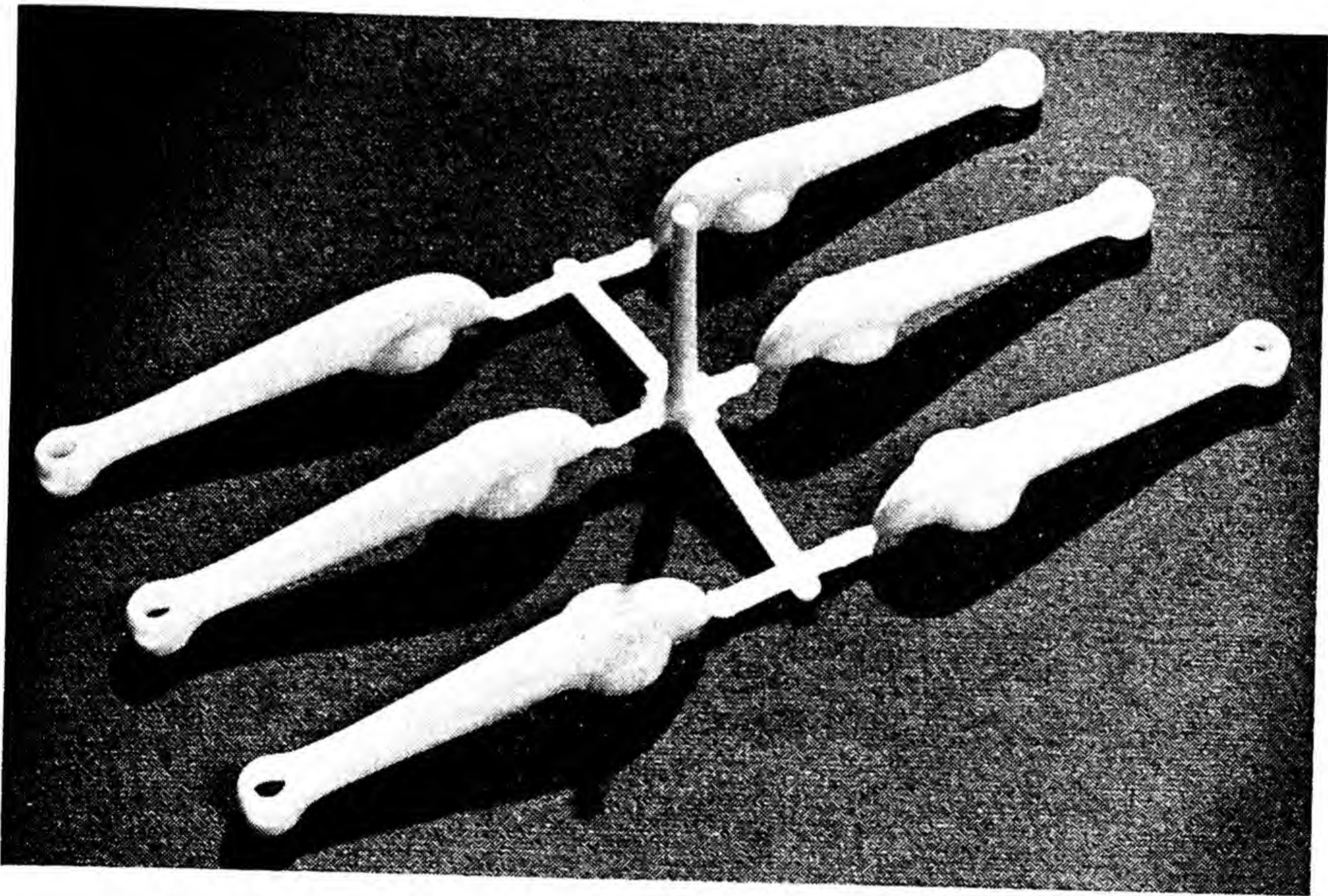FIG. 14.—Injection mold. (*Sobenite, Inc.*)

FIG. 15.—Assembly as removed from injection mold. (*Sobenite, Inc.*)

is taking place, another shot of material is being heated in the plasticizing cylinder.

The successful application of injection molding is often determined by the design of the molds, long before the article is molded (see Figs. 14, 15, and 16). There are a hundred and one "do's" and "dont's" on the proper

design of molds for injection molding. From an operating point of view, sound mold design must take into consideration the following factors: correct gating, uniformity of wall sections, broken corners to facilitate flow of materials, conservative estimates of press capacities in projected area and volume per injection, and the number of cavities that can be used.

Fig. 16.—Finished article produced by injection molding. (*Sobenite, Inc.*)

Transfer Molding.—Transfer molding is a process in which a thermosetting material is subjected to heat and pressure in an outside chamber and then forced into a closed mold cavity where it is cured. It is the
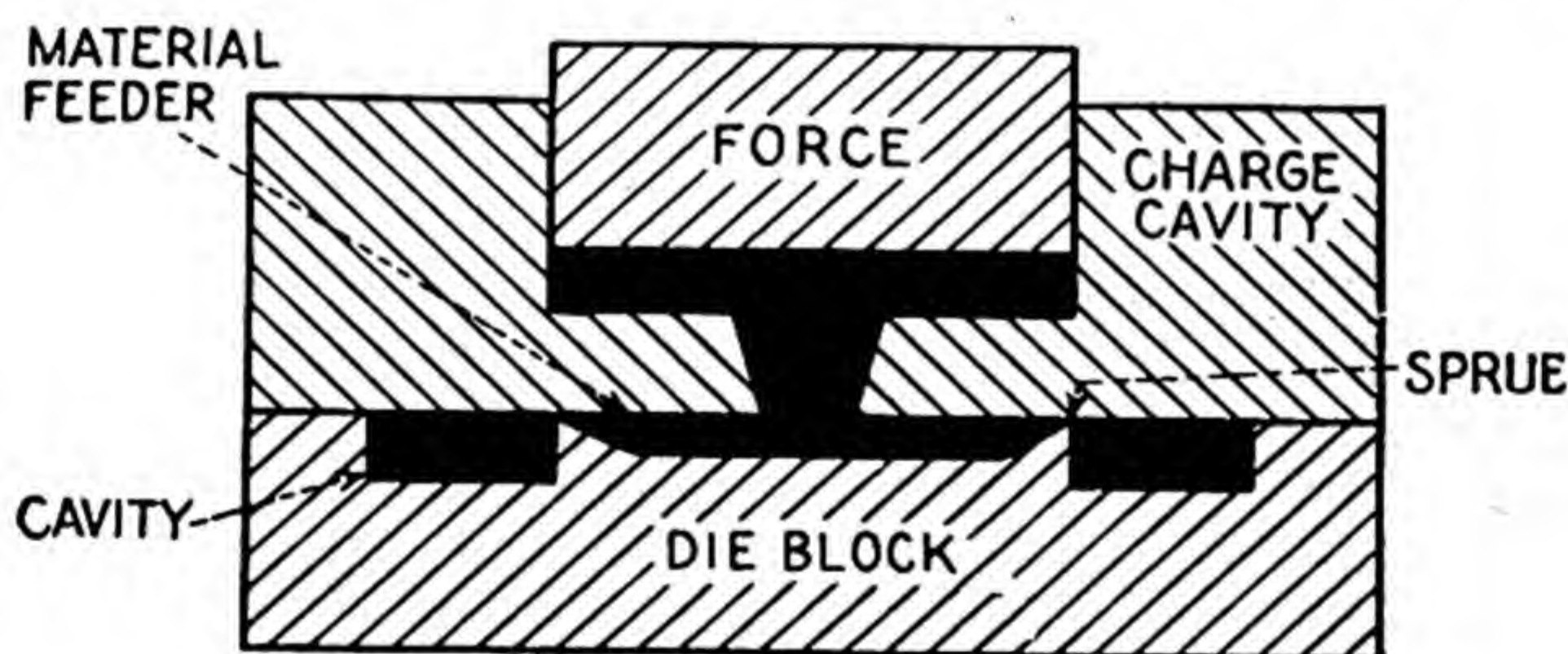

Fig. 17.—Transfer mold.

injection molding of thermosetting materials and differs from injection molding in that the mold is maintained at elevated temperatures and the parts are ejected from the mold without cooling.

This method of molding has many advantages. Because of the ease with which the material fills each cavity, no sudden and excessive strain is placed upon weak projecting mold parts or thin insert pins. Heavy sections of molded parts are filled out with a well-plasticized and partly polymerized material, decreasing the time required for the complete curing of

the piece. Much more delicate and intricate shapes are possible than could be produced by compression molding. Figure 17 illustrates a transfer mold and shows how the material is transferred.

Since the resin is potentially reactive, the correct application of heat and pressure is extremely important. Too little heat and too little pressure cause insufficient flow. Conversely, too much may cause the material to set up prior to reaching the furthest point of the mold, or in extreme cases to set up in the pressure chamber, and jam the machine. The part to be
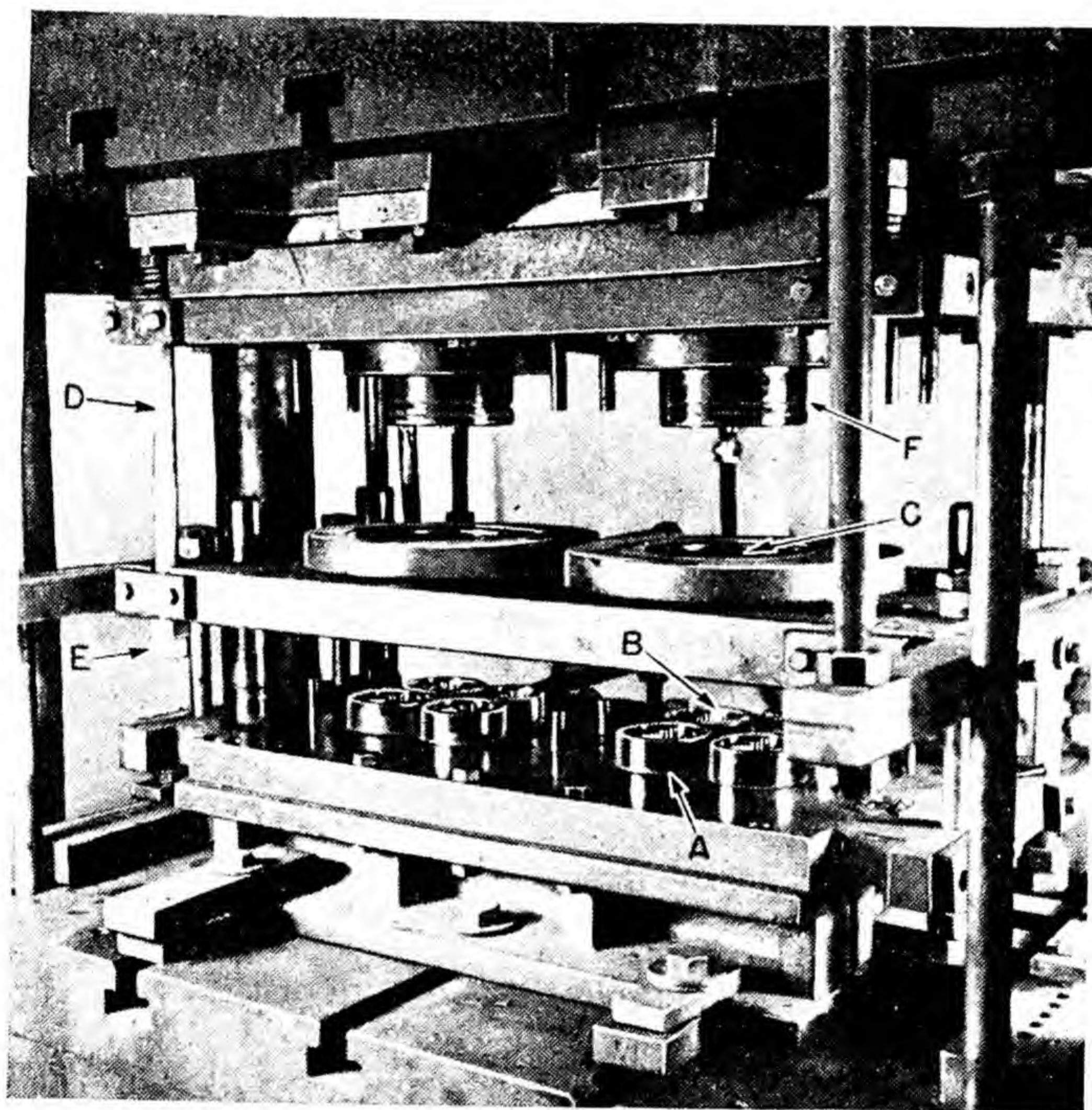

FIG. 18. A press set up for transfer molding. (*Bakelite Corp.*)

molded, the type of plastic required, and the available equipment are the factors that determine the design of the pressure chamber, or chambers, the number and size of gates, the correct heat, the correct pressure, and the design of the mold. In commercial practice today, parts are being manufactured that contain $\frac{1}{10}$ g. to $4\frac{1}{2}$ lb. of material. All types of thermosetting material have been successfully molded by this process.

Figure 18 shows a press set up for transfer molding with an eight-cavity transfer mold divided into two four-cavity sections (*A*). A steel insert (*B*) is positioned in each cavity. Directly above each group of cavities is an injection chamber or pressure pot (*C*), which can move freely on hanger

bolts (D) but is secured from dropping below the illustrated position by restraining nuts (E). The force plugs (F), which force the plasticized molding material into the mold cavities, are attached to the top of the press.

Figure 19 indicates the molding procedure. An operator places preheated preforms in the two injection chambers (A). He then releases the valve-control lever (B), setting the hydraulic pressure system into operation. The bottom of the press rises, lifting the cavities up to the injection-chamber plate (C). As the press continues to rise, the force plugs enter
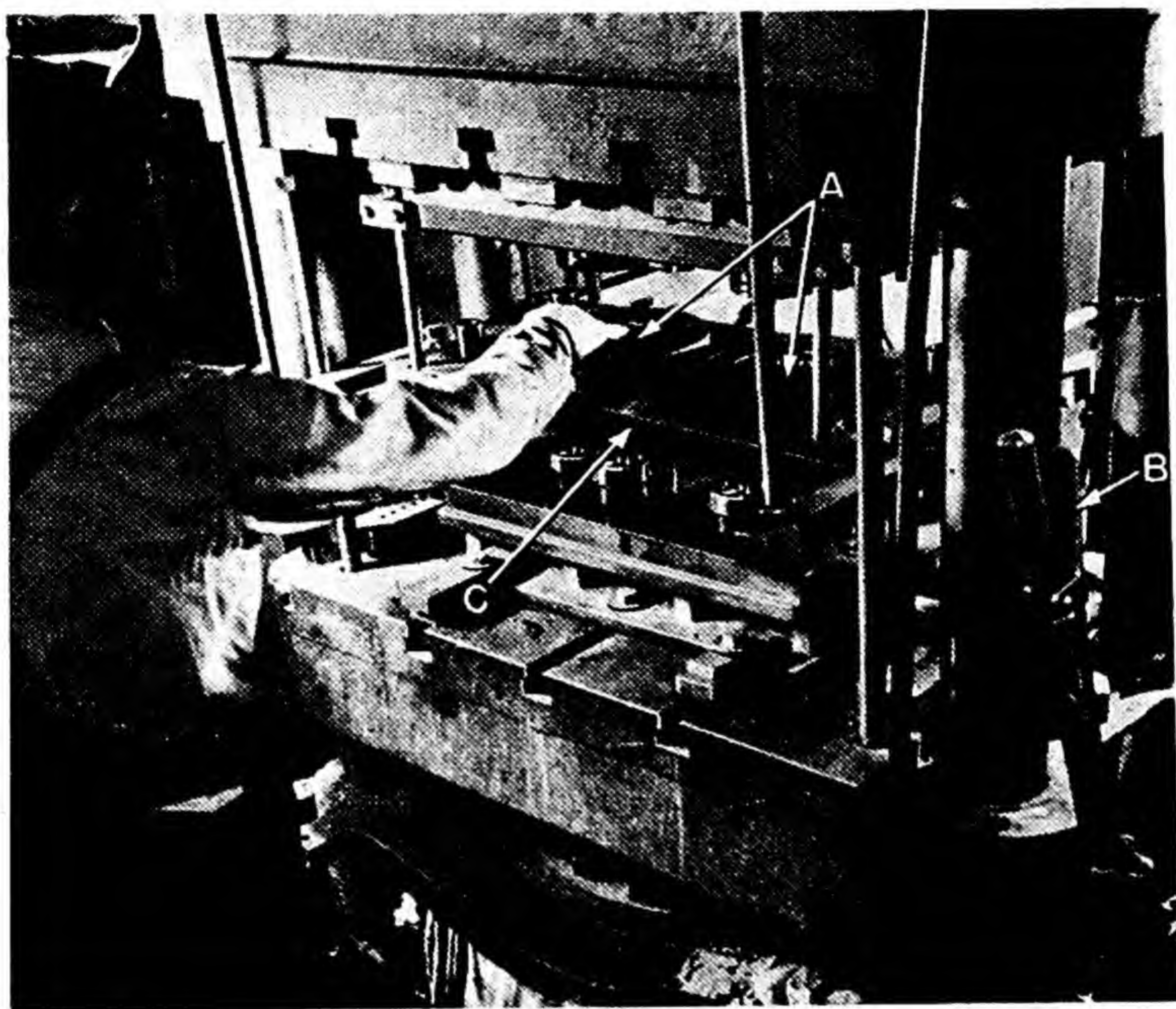

Fig. 19.—Operation of a transfer press. (Bakelite Corp.)

the pressure pots and the heat and pressure plasticize the molding material and cause it to flow into the mold cavities. Since the molds are hot, final polymerization then takes place quickly and smoothly. The press is opened, the molded pieces are removed, and the cycle is repeated.

Jet Molding.—Jet molding has been devised to adapt injection-molding equipment and processes to thermosetting compounds. Thermosetting materials cannot be used in standard injection-molding machines because they cure when heated, causing the material to set up into a solid mass in the heating cylinder. By modification of the heating cylinder and attachment of a special nozzle, it is possible to mold thermosetting materials in injection machines. The heating-cylinder temperature is held below the curing temperature of the compound, and the cylinder serves essentially as

a preheating chamber. The nozzle of the cylinder is surrounded by a ring of metal heated by high-resistance electric coils and cored for cooling. As the injection plunger moves forward, it pushes the molding through the nozzle. Simultaneously, current is applied to the heater ring, which momentarily reaches a high temperature. The heat thus supplied, plus the frictional heat generated by the molding material, plasticizes the compound as it passes through the nozzle. As soon as the stroke is completed, the nozzle is cooled by the passage of cold water, preventing material from lodging in the nozzle. The flow of plastic fills the mold, and the plastic is finally cured by heat supplied in the mold.

Owing to the high fluidity of the molding material at the time it is injected, parts molded by this process are dense, free from porosity, and apparently toughened by the relatively high temperatures employed. Intricate parts with numerous delicate inserts and thin sections are possible with this process. A more uniform quality and a high rate of product are claimed to be other advantages.

Postforming.—This method of forming sheets into various shapes resembles the drawing, bending, and forming of sheet metal. The sheets employed are usually a fabric-base material laminated with phenol-formaldehyde resins. In the forming operation, the material is first subjected to a high temperature for a short period of time, then formed quickly in inexpensive molds and held under light pressure until it sets to the desired shape (see Fig. 20).

Most postforming operations can be done at pressures of 50 to 100 lb. per sq. in., and simple molds and dies made of hardwood, metal, or plastics may be used. Simple bends, channels, etc., are best formed with dies having hinged folding parts on the same principle as bending brakes for sheet-metal working. The choice of material for molds depends on the durability required in production.

The sheets must be formed immediately after heating before the material cools appreciably and loses its formability. Pressure must be retained until the piece cools enough to "set," it in the desired shape. Molds provided with cooling-water ducts cut down the time that pieces must remain in the closed mold.

Quick heating is essential, since slow heating tends to produce blisters and make the material brittle. At 450°F. a $\frac{1}{16}$ in. stock should become pliable enough to form in a period of 45 to 60 sec. Hot plates, infrared lamps, and hot-liquid melts of high-boiling liquids or alloys are used for heating. Ovens are ordinarily too slow and do not give even temperature distribution.

Postforming is a quick, relatively cheap method of forming sheets into a great variety of special shapes, provided the curvature required is not too sharp. The final shape must also be such that it does not require an

appreciable compression or extension of the sheet material.   Even with these limitations, there are many applications of postforming in the production of structural parts.

FIG. 20.—Postformed objects.   (*Taylor Fibre Co.*)

Low-pressure Molding.—The technique of low-pressure molding has become extremely important in recent years.   The development of the bag processes, the production of special resins that cure at low temperatures and pressures, and the rapid increase of experienced personnel during the war period have caused this method to be adapted to the production of molded products that in many instances are superior to similar objects made any other way.   A distinction between low-pressure molding (under 100 lb. per sq. in.) and contact or "no-pressure" molding is sometimes made, but the techniques are identical.

There are two main variations of the bag process.   In one a male mold is made, usually of wood, and sheets of impregnated material are laid over the mold until the desired thickness is obtained.   A rubber mattress is then laid over the mold, and metal or fabric straps are fastened over the bag for additional support.   The bag is then inflated with steam under moderate pressure.   The expansion of the bag exerts a fluid pressure on the laminated material which always acts perpendicular to the surface.   The steam also supplies the heat required for curing.   Phenolic, polyester (particularly the alkyd-styrene type), and urea resins are usually used to impregnate the

sheets, which may be canvas, paper, plywood veneers, glass cloth, or asbestos. Figure 21 illustrates this method of low-pressure molding.

The other adaptation of this process has several variations. If pressure is required, an autoclave must be employed. If a male mold, such as that shown in Fig. 21, is employed, a rubber bag is placed over the whole
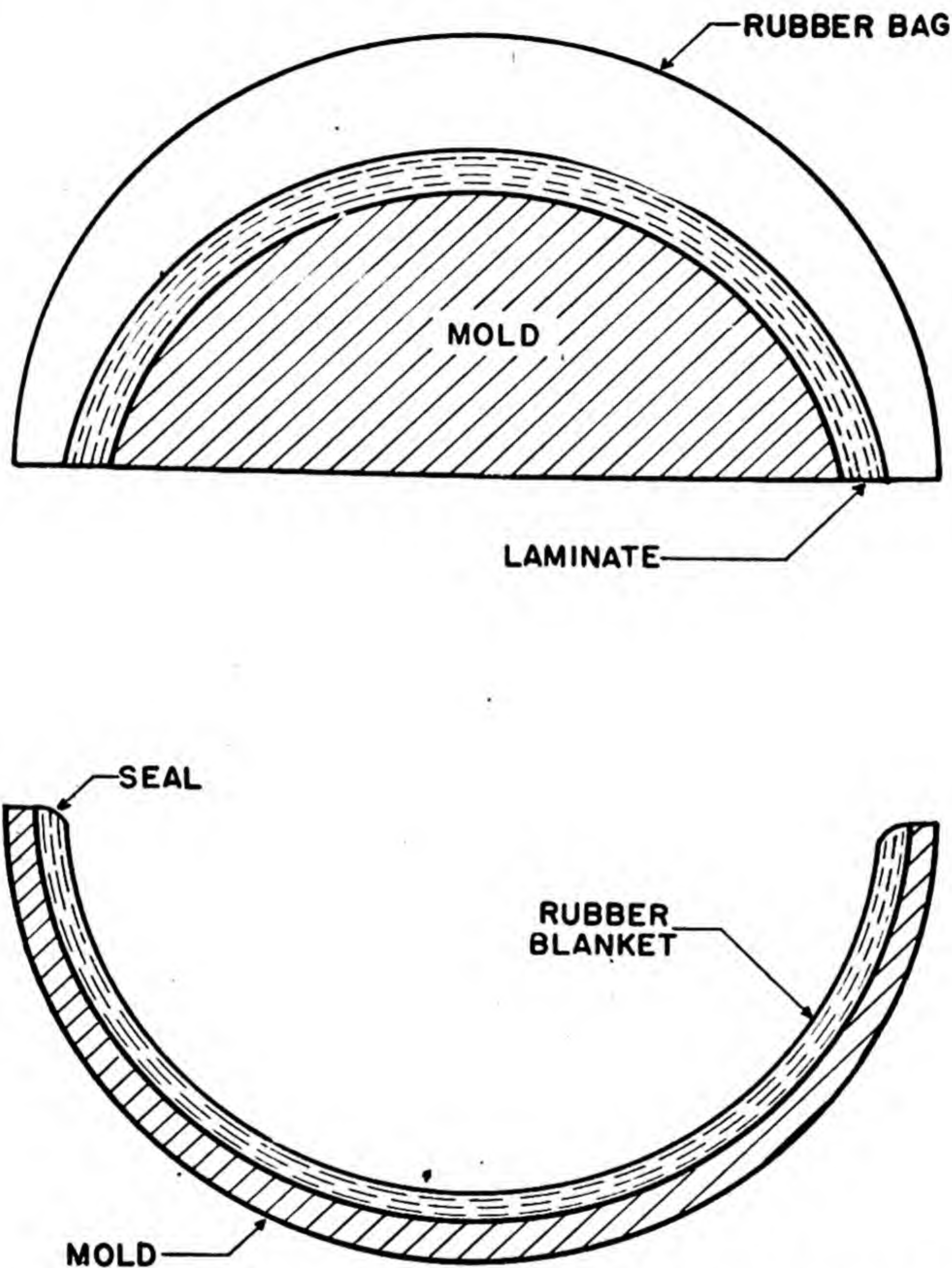

FIG. 21.—Low-pressure molding with rubber bag (above) and with rubber blanket (below).

assembly and the open end sealed, or a rubber sheet is clamped around the edges of the mold (see Fig. 22). Vacuum is then applied to deflate the rubber bag completely and remove all the air from the laminated material. The entire assembly is then placed in a large autoclave and live steam of the desired pressure admitted. After the proper time interval, the assembly is removed and disassembled. This same procedure may be followed when a female mold is used except that a rubber sheet, sealed to the edges of the mold, must be used rather than the mattress bag. Molds of this
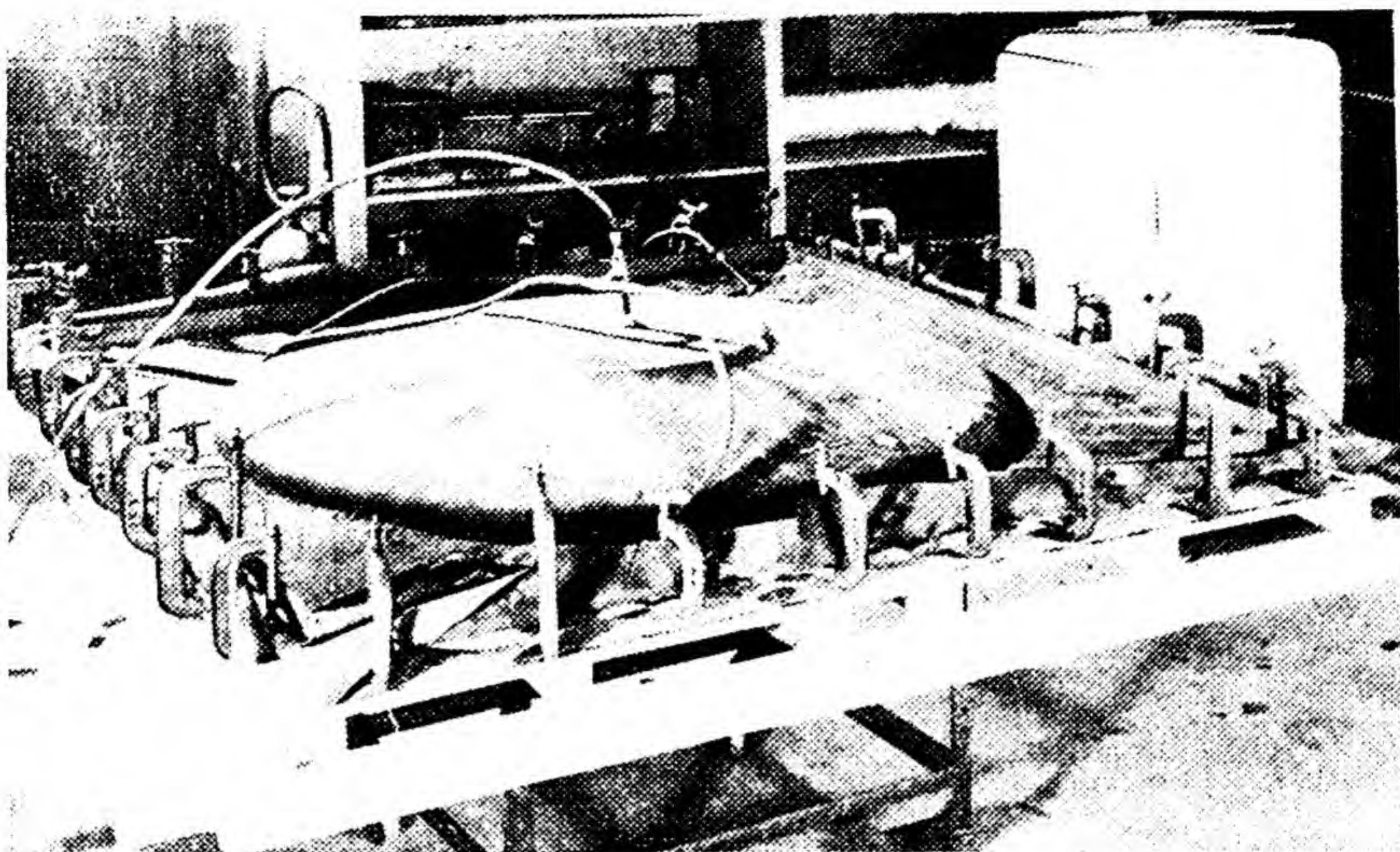
FIG. 22.—Low-pressure process applied to the molding of a reinforced plastic tank dome showing vacuum connections and method of sealing edges of rubber blanket. (*Owens-Corning Fiberglas Corp.*)
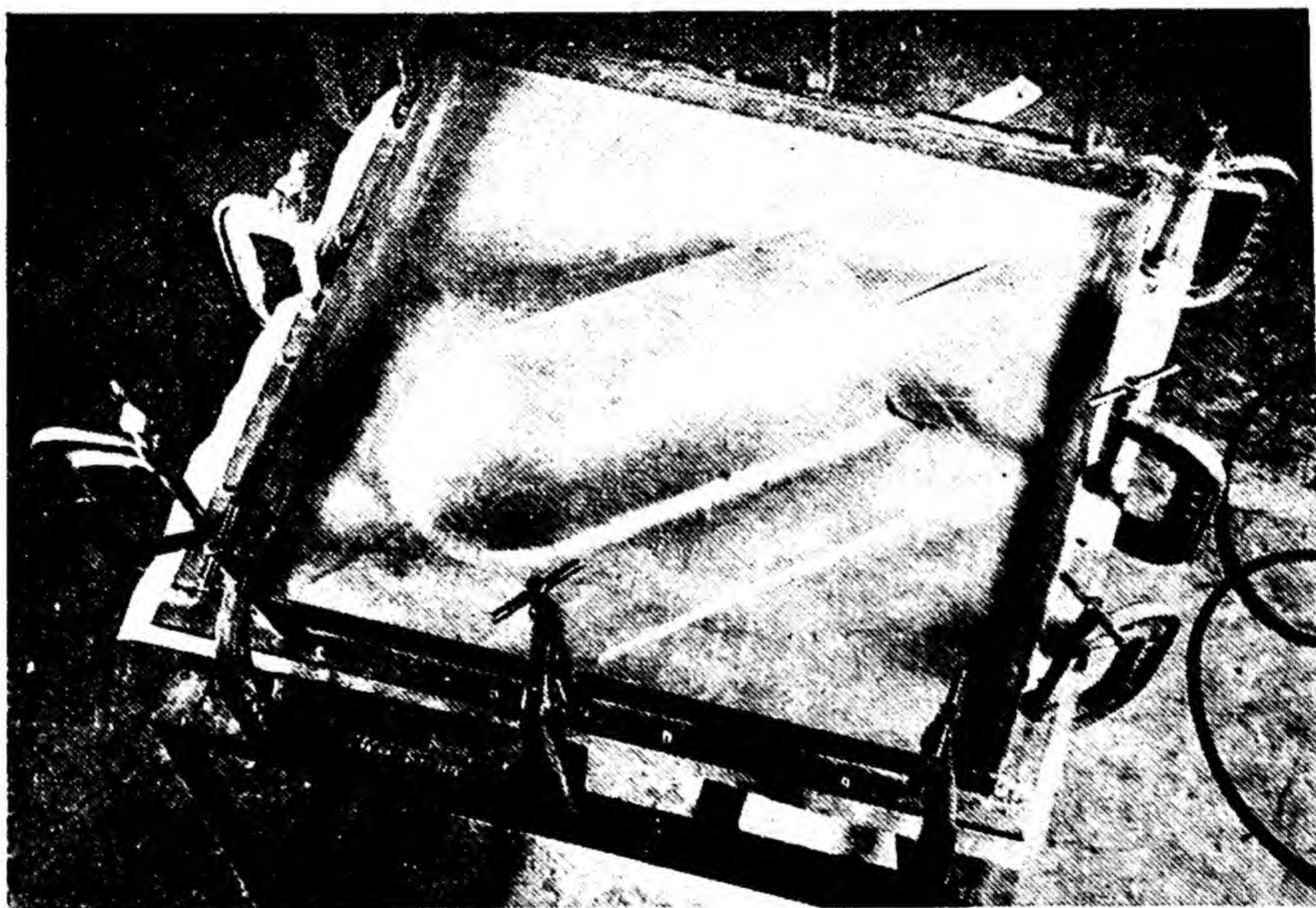

FIG. 23.—Low-pressure assembly ready for the final cure. (*Owens-Corning Fiberglas Corp.*)

type are ordinarily made of various metals, but wood and plaster of Paris are becoming more and more important. The small molds may be made of hollowed-out blocks, while the larger sizes are formed of sheet metal.

Variations in this method of molding are being constantly introduced. New resins having the proper viscosity and tackiness are reducing assembly problems. Pressures and temperatures required for curing are also being reduced. The "no-pressure" variation merely requires the application of vacuum behind the rubber bag and a cure in an oven rather than an autoclave (see Fig. 23). This is an important advantage in that the simplest types of air ovens may be used, requiring a minimum of auxiliary equipment. Cores can be made out of sand enclosed in cellophane or polyvinyl alcohol sheets. These permit easy removal of a core after molding. A great variety of relatively inexpensive plaster-of-Paris, wood, or metal split molds and cores have been developed for complex shapes.

When rubber is used as a bag material, a considerable proportion of the total labor involved is required to remove wrinkles, which will be transferred to the surface finish of the molded article. This difficulty can be eliminated by the use of comparatively thin polyvinyl alcohol sheeting. In this case, the wrinkles are not transferred and the surface is not marked. However, smooth, polished surfaces can be obtained only on the mold side. The bag side of the object has a rougher surface, similar to the rubber.

A recent development in laminated products, made without employing pressure, has been the use of thermoplastics in the fabrication of containers, boats and airplane structures. Burlap or canvas, cut to the desired pattern, is dipped in a dope of cellulose acetate containing plasticizers, dried, and then laid on a wooden form or mold. It is then sprayed with an acetate lacquer, and another layer of impregnated fabric is added. Layer after layer is built up in this manner. As the solvent evaporates, a large amount of shrinkage occurs, producing an article of great strength and high density. This method avoids the use of expensive molds and forms, and no heat or pressure is necessary.

The use of glass cloth as a laminating material is becoming more and more important. The glass cloth is easy to assemble, strong, and completely inert to weathering and most chemicals. It forms an extremely strong laminate. The use of fibers in place of cloth is another adaptation of this process that appears promising. At the present time, glass, jute, and sisal fibers are used for this purpose (see Fig. 24). Because glass fibers will not absorb moisture, they will neither shrink nor swell under changes in moisture conditions. In addition, they possess a low coefficient of thermal expansion and are strong enough to resist normal expansion of the resin.

The ability to obtain directional properties by the use of fibers is a great advantage in design. If stresses to which the product will be subjected

occur in several directions, it is possible to distribute the fibers in these directions, in proportion to the amount of stress in each direction. Or, if the principal stress is to come from one direction, it is possible, by arranging

FIG. 24.—A small boat with a hull built up of rope fibers with a canvas exterior, molded by a low-pressure process. (*Winner Manufacturing Co., Inc.*)
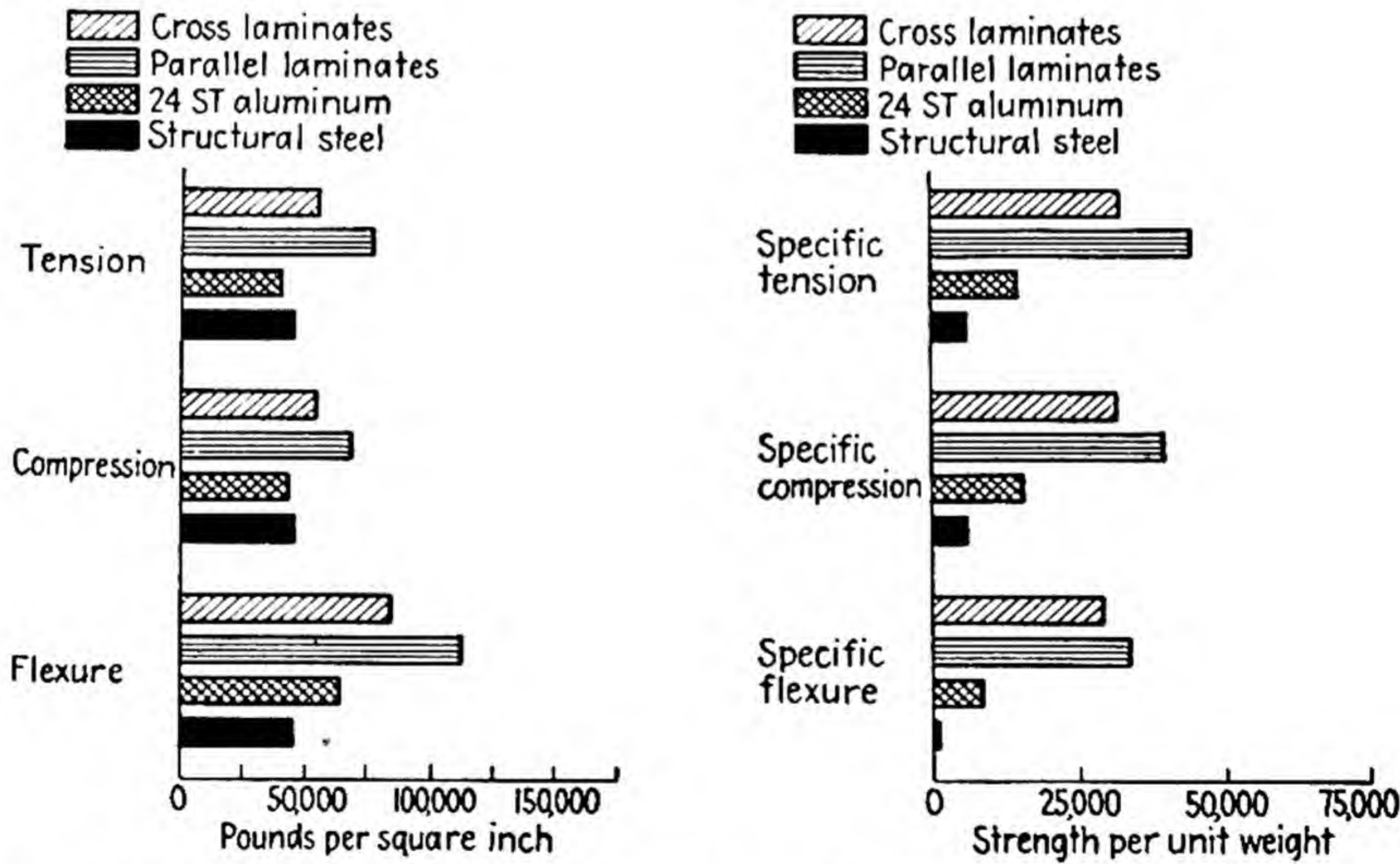
FIGS. 25 and 26.—Comparative properties. (*Owens-Corning Fiberglas Corp.*)

the fibers in the direction of stress, to exceed the strength of structural metals.

The accompanying charts (Figs. 25 to 28) show the strength properties attainable with cross-laminated and parallel-laminated glass-plastic lami-

nates, as compared with corresponding properties of 24-ST aluminum and structural steel. Values are based on laminates made with heat-treated unidirectional glass cloth and a representative low-pressure resin molded at 15 lb. per sq. in. pressure. Specific strengths are original strengths divided by the specific gravities of the materials, except for specific flexural strength, which is obtained by dividing by the specific gravity squared.[1]
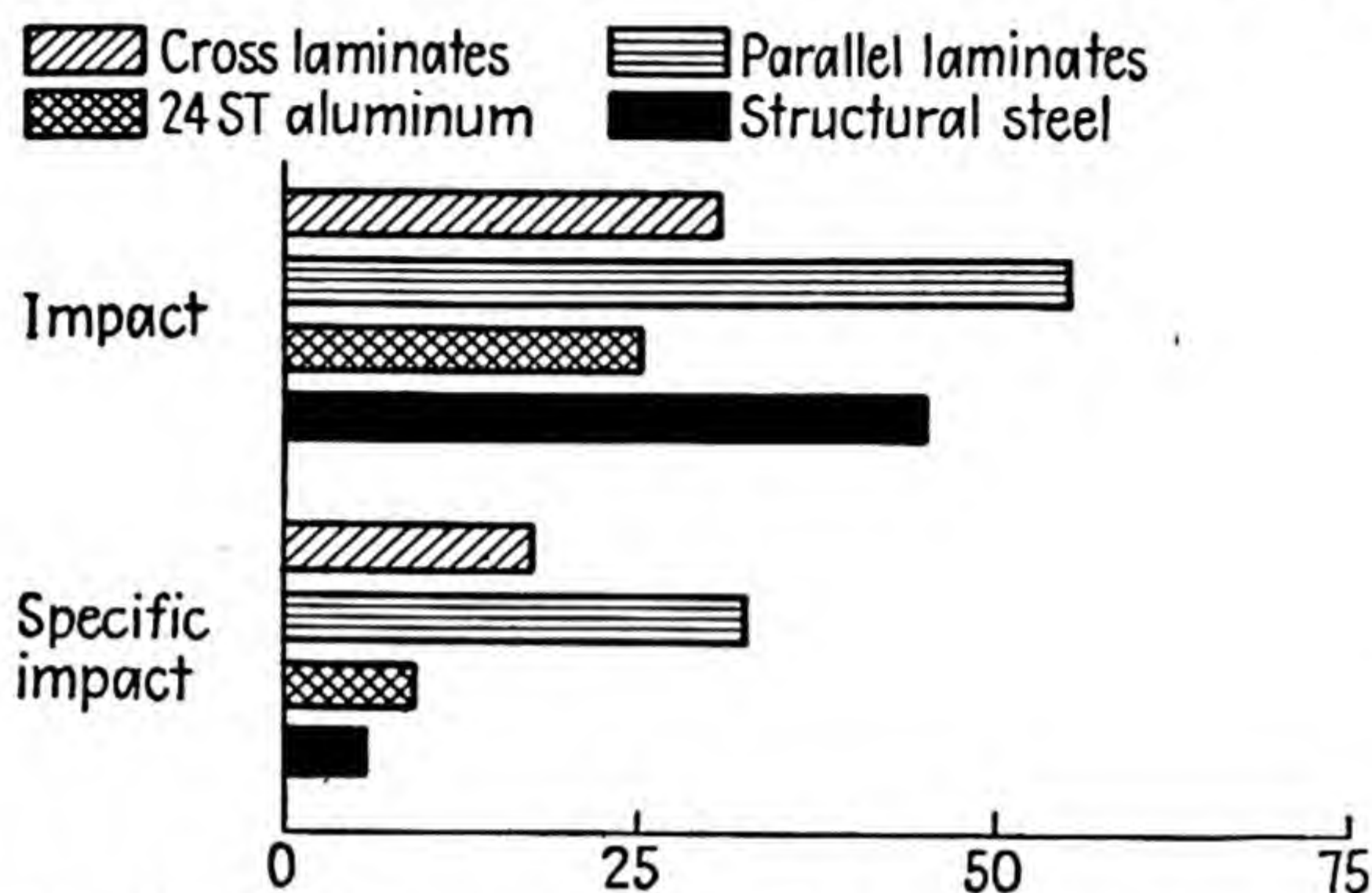

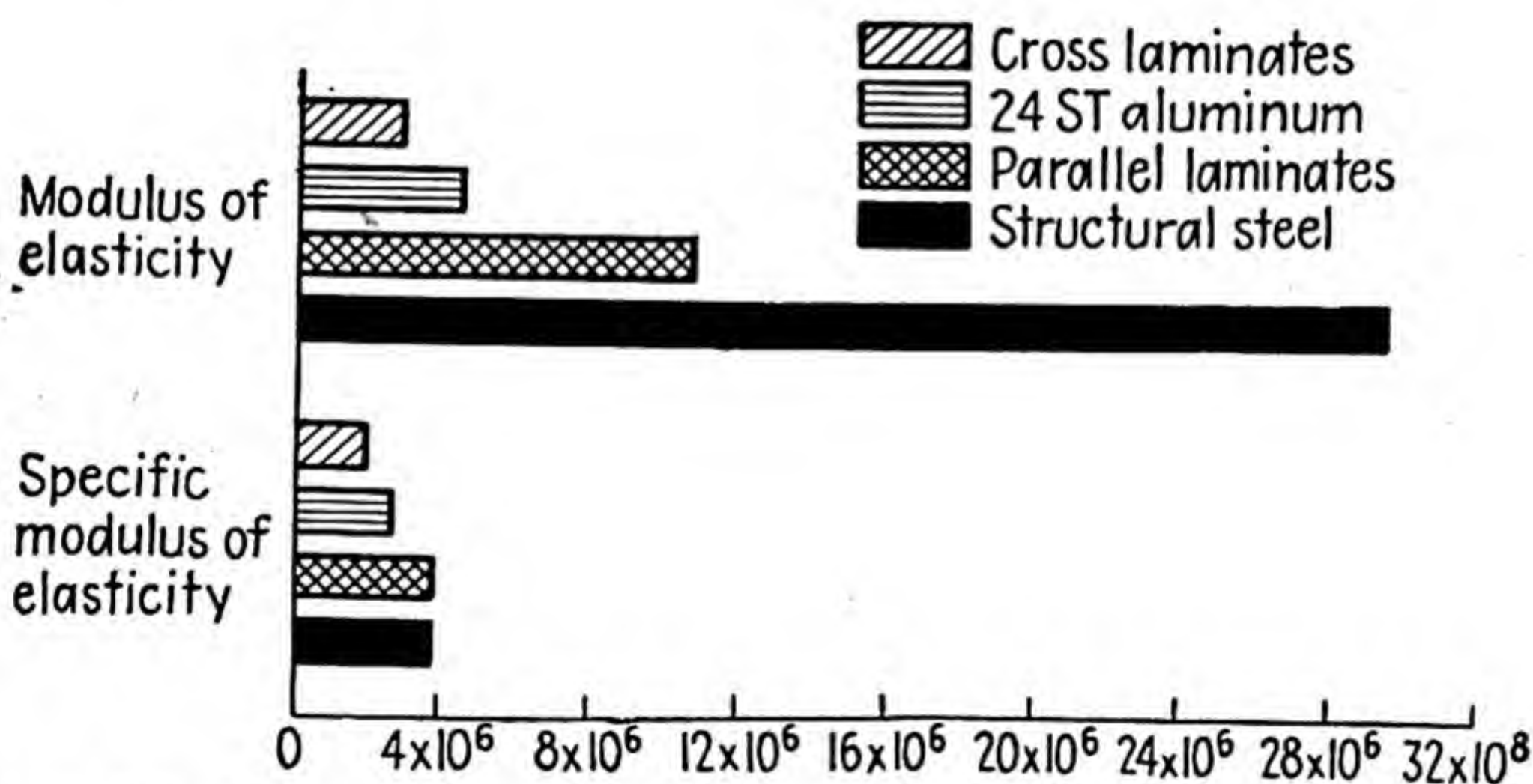FIG. 27.—Comparative properties. (*Owens-Corning Fiberglas Corp.*)

FIG. 28.—Comparative properties. (*Owens-Corning Fiberglas Corp.*)

In metals, the modulus of elasticity is not variable, but the modulus of glass-plastic products is controllable over a wide range. This control of the modulus is a function of the amount of glass and of the weave and orientation of the glass cloth used for reinforcement.

Glass-plastic laminates have good dielectric strength. They have no definite yield point, so it is possible to work the material very close to its ultimate strength without permanent deformation. The same characteris-

[1] SLAYTER, G., and H. W. COLLINS, paper presented at December, 1945, meeting of the American Institute of Chemical Engineers, Chicago, Ill.

tic prevents the material from denting when struck a sharp blow.   Because of its fibrous structure, and the consequent scattered distribution of any imperfections, the material will not propagate cracks.

The use of fibers makes production easier since they can be formed into a mat.   It is possible to preform the coated fibers by the use of vacuum filter forms as can be done in the papier-mâché process.
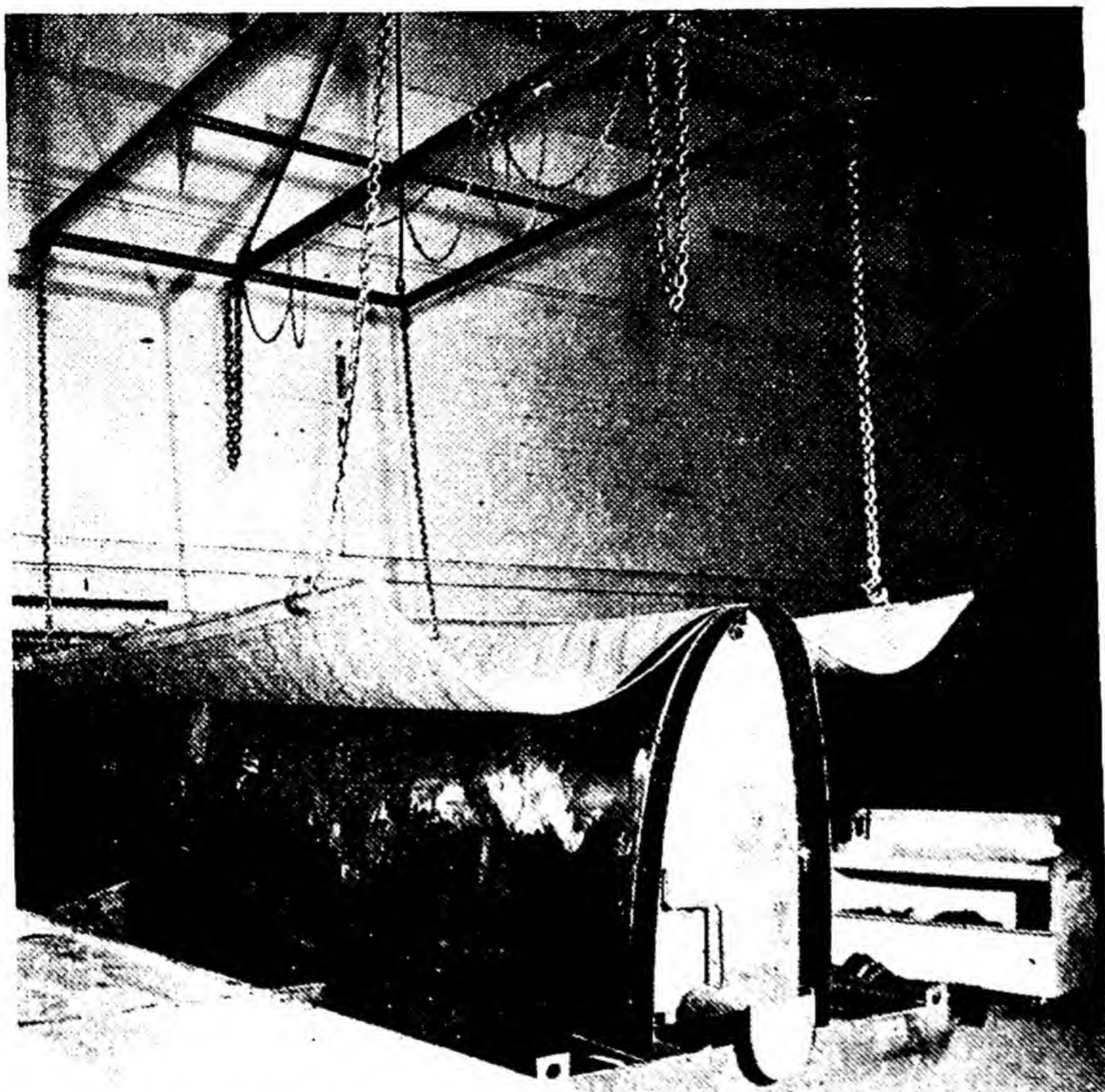

FIG. 29.—Laying wooden veneers on an airplane-wing form for low-pressure molding. (*Bakelite Corp.*)

The importance of low-pressure molding cannot be overstressed.   The molds are cheap and, for this reason, can be used for the production of a minimum number of pieces.   In this respect they are comparable to the use of patterns in a foundry rather than to compression molds.   In addition, relatively expensive molding presses are not required so that the initial outlay for equipment is very small.   This process is particularly adaptable as an adjunct to woodworking mills of various types, such as furniture plants, and small boat construction.   All the finishing equipment and skill required is usually available in these plants, and the additional technique required for this molding process is not too difficult to acquire.   The various possible adaptations of this process together with the use of the newer

types of resins give promise of causing remarkable changes in the fabrication of many products ranging in size from hats to 50-ft. boats. Boat hulls in the 30-ft. range are already in production, and entire airplanes are assembled by gluing together various parts made by this process (see Fig. 29).

It is possible to produce articles of almost any size and shape. Fenders, automobile bodies, boat hulls, ducts, and various tortuous shapes have all been produced by this method. The strength-weight ratio in all cases is better than that obtainable by any of the metals. In addition, excellent impact resistance is obtained.
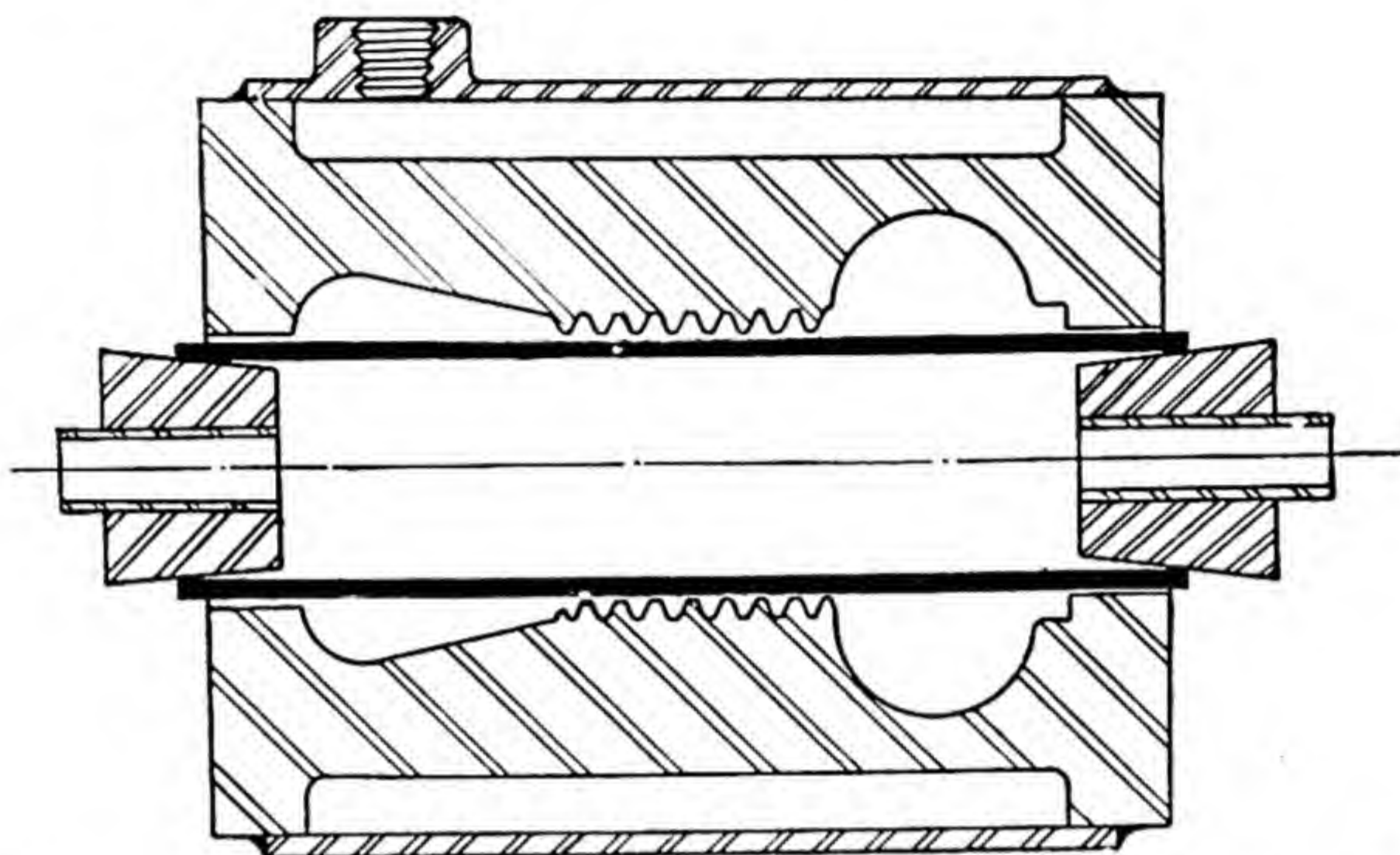

Fig. 30.—Cross section of a mold for blowing tubing. (*Modern Plastics.*)

A wide variety of finishes for these objects has been produced. A colored or a pigmented resin can be used to produce the finish. The resin is placed in an outer layer of cloth and bonded and cured in the molding operation. The outer layer of cloth can also be printed, just as other textile materials are dyed and printed, and the color is protected by the resins used for bonding. Various lacquers have also been used for spray coating, and flexible coatings that will not fail even under high impacts are available.

Blowing.—The first and oldest method of blowing plastics is the expansion of plastic sheets by the introduction of air or steam between sheets while they are clamped between the halves of a mold, a technique dating back to the early manufacture of hollow celluloid articles. Although this method of fabricating plastics is frequently overlooked, it is widely used.

In the oldest application of this process, sheets, partly expanded by internal pressure, are clamped between the mold halves where pressure and heat nip and fuse the edges and steam is used for blowing. This method leaves a fin around the object which must be removed in finishing operations. A variation of this method consists of the use of an extruded tube in place of the conventional sheet (see Fig. 30). The section of tube is softened and placed between two halves of a mold. Steam or some other suitable heating medium is introduced under pressure through a metal

insert, which is placed in the upper end of the tube to support it. The pressure forces the plastic to expand and, when it is evenly heated, to take the shape of the finished mold. As the mold closes, the bottom of the mold clamps the lower end of the tube and also nips off an unused portion so as to produce a smooth internal and external finish. Containers with screw-cap closures can be readily produced by this method. The relative simplicity of this type of blow molding may well lead to the development of a continuous process.

A third method of blowing thermoplastics (see Fig. 31) is related to the

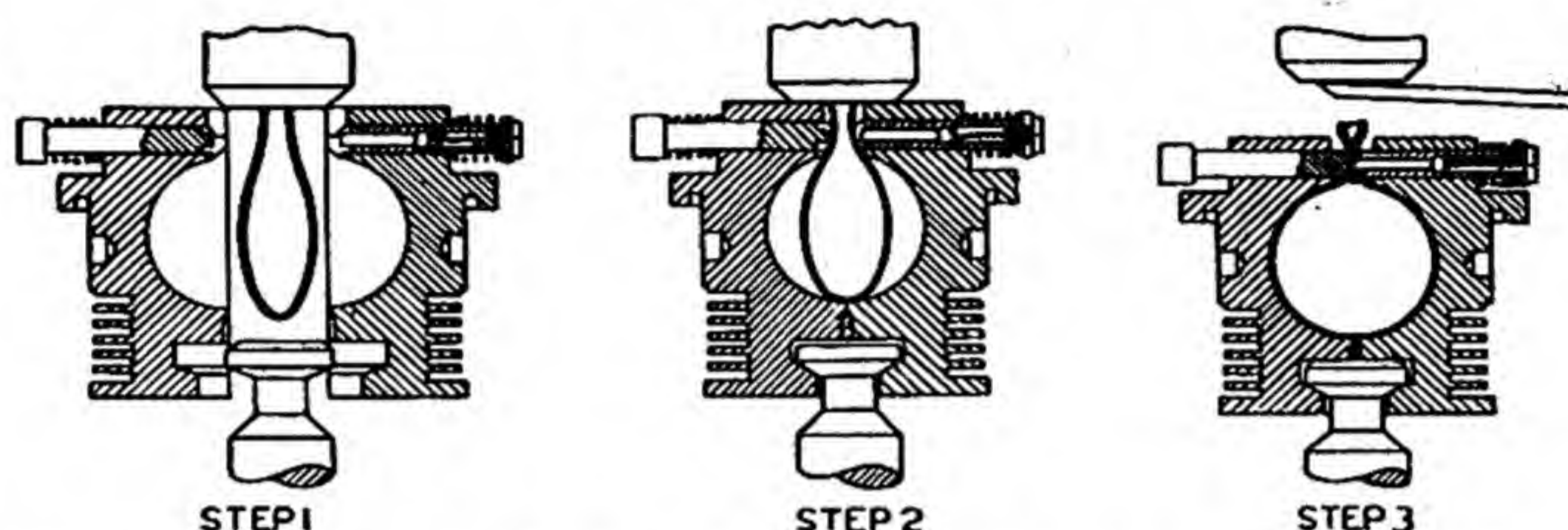STEP 1   STEP 2   STEP 3

FIG. 31.—Three steps in the blowing of a small sphere. (*Modern Plastics.*)

extruded-tube process. It is used in the forming of hollow closed articles such as decorative Christmas-tree balls, floating toys, and toilet ball floats. This process utilizes an extruder in which the plastic is softened and prepared for molding. As the plastic is extruded, air is introduced. Since the end of this softened plastic tube has been collapsed and sealed in the forming of the previous piece, the extrusion begins to swell. At this point, an open mold closes on the swelling tube and the object is formed by blowing the plastic material into the mold cavities. The blown plastic is nipped off, and the rotary table moves on one station, permitting some cooling. The hollow article is expelled from the mold when it finally opens at the discharging station. The process is similar to the operation of the bottle machines in the glass industry.

Plastic containers produced by this process are considerably lighter than glass containers of the same size and shape (see Fig. 32). A plastic bottle weighs approximately one-third as much as a glass bottle.[1] In addition, because of thinner sections, the plastic bottle occupies less space. If polystyrene is used as the plastic, the bottle can be used for hydrofluoric acid and strong alkalies. Good strength characteristics can be obtained. The cellulose acetate or acetate-butyrate containers are better in this respect as well as in resistance to shattering.

A fourth type of plastic blowing involves the expansion of injection-molded blanks while they are still hot. In this method, a blank is injected into a hot mold around a heated hollow core or insert. After injection,

[1] GRIFFITH, H. E., *Modern Plastics,* **21,** 79 (1944).

the hot lump of plastic is removed from the injection machine and placed in a cold mold. Air at about 80 lb. per sq. in. pressure is introduced through the hollow core, and the plastic is expanded into the mold cavities. If temperature conditions are carefully controlled, it is possible to produce hollow articles of almost any description. This blowing method opens up
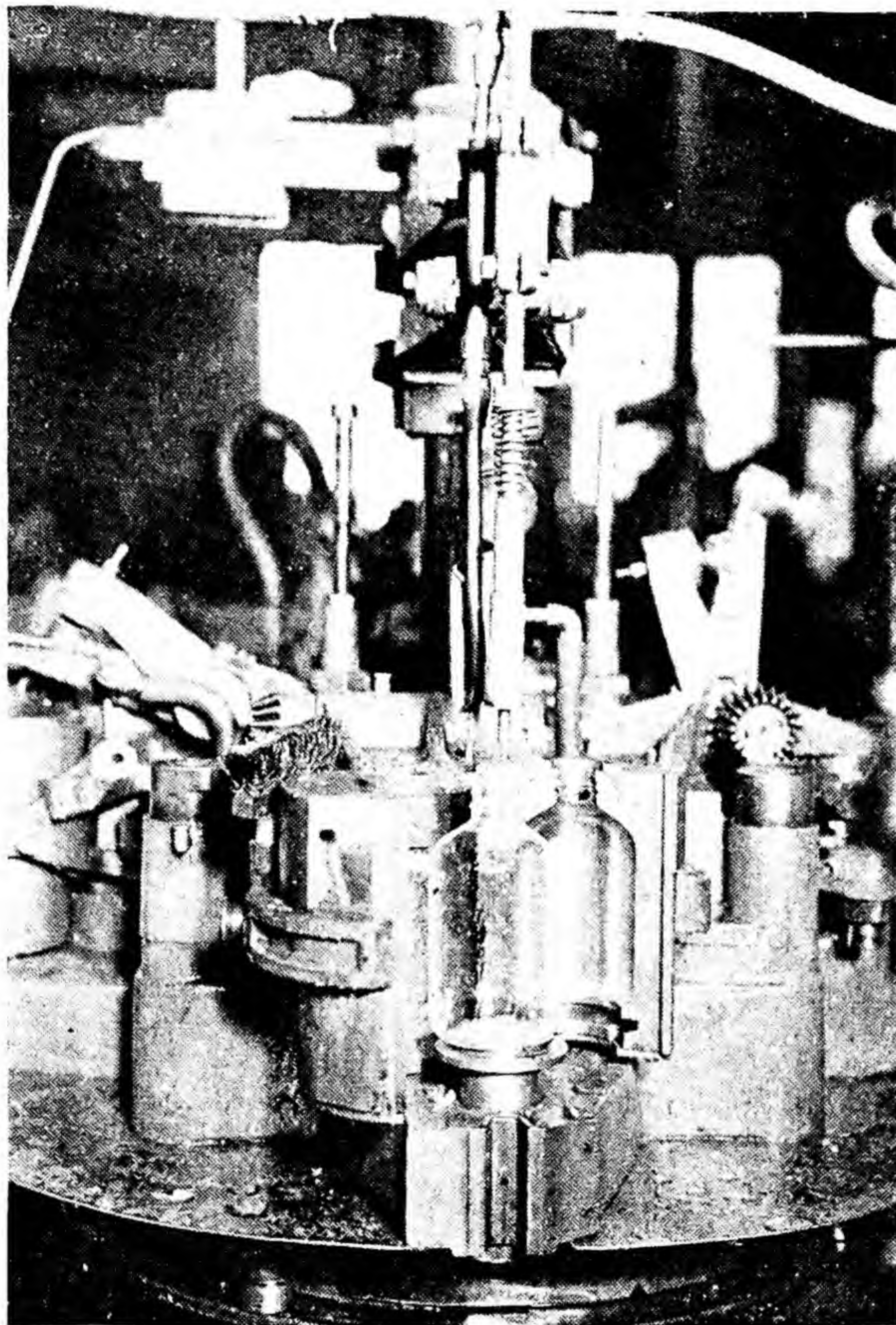

FIG. 32.—A plastic bottle emerging from the mold after blowing. (*Plax Corp. and Modern Plastics.*)

many possibilities for new uses of plastics which could not be attempted in the past without molding the parts in halves and cementing them together.

Blow molds may be made of cast iron, aluminum, or some other inexpensively worked material, which allows lettering and designs to be reproduced at low cost. The list of items that can be made by this method is constantly being extended. At the present time, the cellulose derivatives

and polystyrene are the most widely used plastics in this process, but experimental work indicates that many other plastics may be formed by this process.

Casting.—At the present time there are three important applications of the casting process in the forming of plastics: the casting of phenol-formaldehyde resins in special molds, the formation of sheets and rods and special shapes of acrylic and allyl resins by a special casting process, and the production of large punches and blocks by casting either ethyl cellulose–wax mixtures or specially plasticized acetate-butyrate.

In the production of cast articles of phenol-formaldehyde, the polymerization is stopped at the *A* stage, where the thermosetting resin is still fusible and fluid enough so that it will flow readily into the recesses of a mold. Lead molds, made by the dipping process, are usually employed. The resin is poured into the mold and taken to carefully regulated ovens for the final curing process. The cure takes place at a controlled temperature in the range of 60 to 75°C. At this temperature the time required is of the order of magnitude of days and weeks, depending on the thickness of the various sections.

Both semifinished objects and sheets, rods, and tubes are produced by this method of casting. In many cases, the finished piece may be cut from a more massive casting. Thus coat hangers have been cast in one lump and then sliced off, much as pieces of bread are sliced from a loaf. A characteristic of polished cast phenolic resins is the beautiful luster and excellent color effects that can be produced. These properties make this process important in the production of materials for novelties and decorative articles. The details of the process are given on page 138.

The casting process as applied to acrylic and allyl resins differs from normal casting processes in that considerable polymerization is required for hardening. In the casting of phenolics, the final hardening of the fluid resin also depends on polymerization to establish the cross linkages required, but the amount of polymerization required was relatively small. In the case of the acrylates, the monomer itself, or a viscous liquid prepared by the careful mass polymerization of the monomer to a low degree of polymerization, is used for casting and the entire hardening process is due to the polymerization reaction. This method of casting is used to produce clear sheets up to 2 in. in thickness and in sizes up to 36 by 48 in. Rods and cylinders are also produced as stock items, and various special shapes are possible.

The methods used to cast these resins are relatively simple, but care is required to obtain the necessary close control of time and temperature. A catalyst, such as benzoyl peroxide, is dissolved in the monomer, usually at temperatures not over 70°C. The catalyzed monomer is then carefully poured in the mold in such a manner as to avoid the entrapment of air

bubbles. If any bubbles do form, they must be allowed to rise to the surface and break before the final curing takes place. The exclusion of air bubbles is one of the most difficult technical problems in the casting of these materials.

These materials reproduce the mold surfaces against which they have been cast, so that highly polished surfaces can be obtained by the use of polished glass or metal molds. This is particularly important where high clarity and good optical properties are desired. Densely cast plaster-of-Paris molds that have been coated with lacquer and subsequently lubricated with mineral oil are also used. Low-melting alloys such as Wood's metal or rose metal are used when objects having undercuttings or reentrant angles are to be cast. In using this type of mold, the polymerization is carried out at a relatively low temperature. The metal can be easily removed after polymerization by melting in hot water.

The casting of highly plasticized thermoplastic resins by the use of a hot liquid melt followed by cooling in a manner exactly analogous to the casting of metals has been limited to cellulose acetate-butyrate and ethyl cellulose-wax mixtures. In this process, no additional polymerizaton takes place. Up to the present time, these cast thermoplastics have been applied almost exclusively to the production of various types of tools, such as punches, blocks, jigs, and fixtures. Different blends are compounded for different uses.

In the production of these products, simple wooden or plaster-of-Paris molds can be used. The inside surface can be lined with cellophane or tin. If punches are to be made, they can be force fitted into metal dies by heat and pressure. This method of making punches and jigs has been developed by the aircraft industry, where largely it has proved to be a great timesaver when compared with the use of lead punches or shaped wooden fixtures, particularly in the forming of sheet aluminum.

STANDARD SHAPES

The production of sheets, rods, tubes and tubing, angles, and other special profile shapes has become an important application of plastics. Four general processes are used to produce the various stock shapes. They are extrusion, laminating, casting, and blocking and sheeting. Almost any shape for which a die can be formed is made by extrusion. Laminating is used to make sheets, rods, tubes, and angles. Casting is important mainly for sheets, rods, and tubes, particularly in the fabricating of methyl methacrylate resin. Short tubes, rods, and special shapes are made in the casting of phenolic resins. Since casting was discussed under molding, no further discussion is necessary in this section. Blocking and sheeting is used to produce sheets of cellulose plastics.

Extrusion.—The so-called "dry-extrusion method" utilizes thermoplastic molding powders and relatively small extrusion machines similar to those long employed by the rubber industry. Dry-extrusion machines consist essentially of a hopper, a screw-feed mechanism or a hydraulic ram, a heating chamber, a nozzle, and a die. The powder is stored in the hopper and falls by gravity into the screw feed where it is forced forward through the heating chamber, the nozzle, and finally through the die from which it emerges with a cross section roughly resembling that of the die. The extruded form is picked up at once by a conveyer belt and then passes under cooling blasts of air. Figure 33 shows a general arrangement of extrusion equipment.

Many of the steps involved in this process are subject to regulation, and the art of extrusion is anything but standardized. Those who are success-
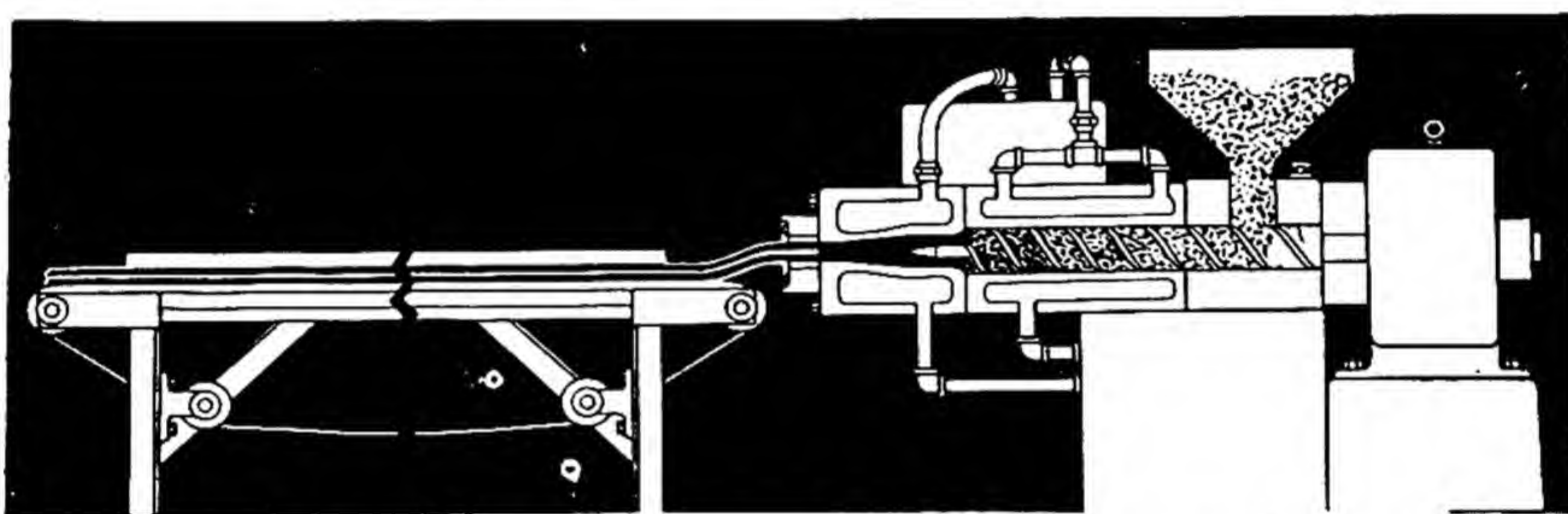

Fig. 33.—Diagram of an extrusion machine and cooling table equipped with an endless belt.

ful at extruding complicated shapes have hit upon the actual method used by a long process of trial and error.

The clearance between the screw and wall of the cylinder is extremely important because of the relation between this clearance and the extrusion pressure developed. The materials of construction of the screw and barrel must be chosen to withstand severe mechanical forces and should exert no specific catalytic effect on the decomposition of the compound being extruded. Cylinders made of hardened corrosion-resistant ferrous alloys are most desirable. The screw is usually made of tough and rigid steel and is chromium plated on all frictional areas but not on the lands that may contact the walls if the screw deflects appreciably. Optimum rotational speed of the screw varies for different die shapes, sizes, and compounds, and for this reason variable-speed drives are usually used.

Laminating.—In the manufacture of laminated sheets, rods and tubes, resin-impregnated paper, fabric, or wood is integrally bonded together by the adhesive action of the resin. In this respect, it closely resembles the low-pressure molding process, except that since standard shapes are produced in large quantities it is possible to use more expensive molds and hot-press methods. This also makes it possible to employ resins that re-

quire higher temperatures and pressures and are, at least for many applications, considerably cheaper. Since plywood is normally produced in flat sheets, it is included in this description of the production of standard shapes.

Plywood is composed of several layers of veneer or wooden layers of appreciable thickness bonded together in a "sandwich" construct on by various resins. If wooden boards are included as core materials in the sandwich, as distinguished from veneers, they are laid with the grain run-
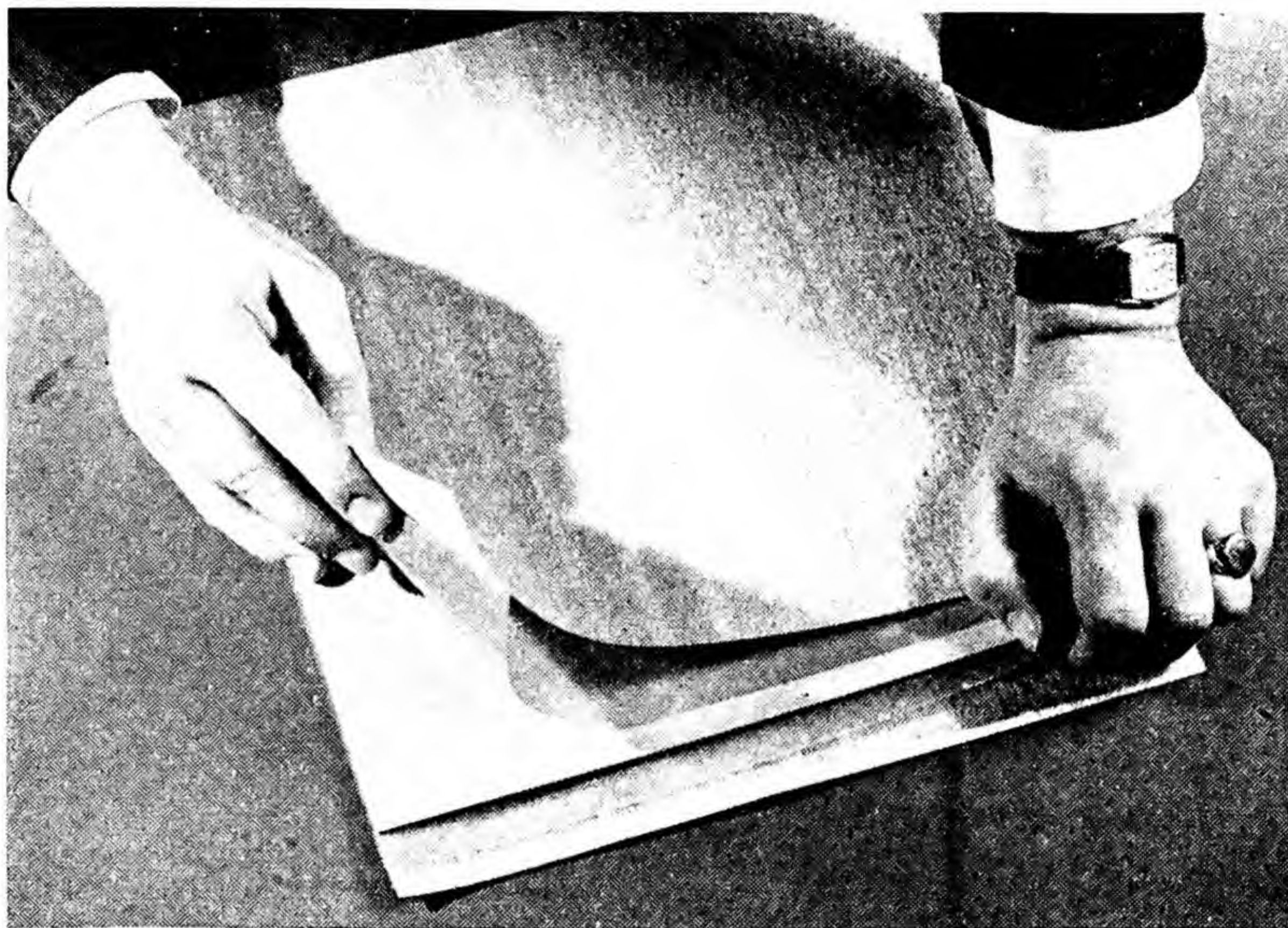

Fig. 34.—Interleaves of resin-impregnated tissue paper between layers of veneer prior to the curing operation in the formation of plywood. (*The Resinous Products & Chemical Co.*)

ning crosswise to each other so that the resulting plywood has a more nearly uniform strength in all directions than does a board of equal thickness.

In the plywood-manufacturing process, the resin can be applied as a solution or a powder, but it is usually used in the form of resin-impregnated tissue paper interleaved between the various wooden layers (see Fig. 34). This method permits greater speed in assembling and gives a more uniform resin distribution, with a resulting increase in uniformity and strength.

The assembled layers are then inserted into a hot press having multiple openings and steam-heated platens. These presses have as many as 20 openings and range in size up to 100 by 150 in. Normal pressures range from 125 to 250 lb. per sq. in., and temperatures of 275 to 300°F. are employed. The time in the presses will vary from 5 to 20 min., depending on the thickness of the panel (see Fig. 35).

The use of high-frequency methods of supplying heat is a recent development. This method employs a high-frequency electrostatic field between electrodes inserted between the sheets of plywood. The rapidly reversing electrostatic field generates heat within the wood and resin layers. Since the heat is generated uniformly thoughout the mass where it is required, rather than being supplied from the surface, much better uni-
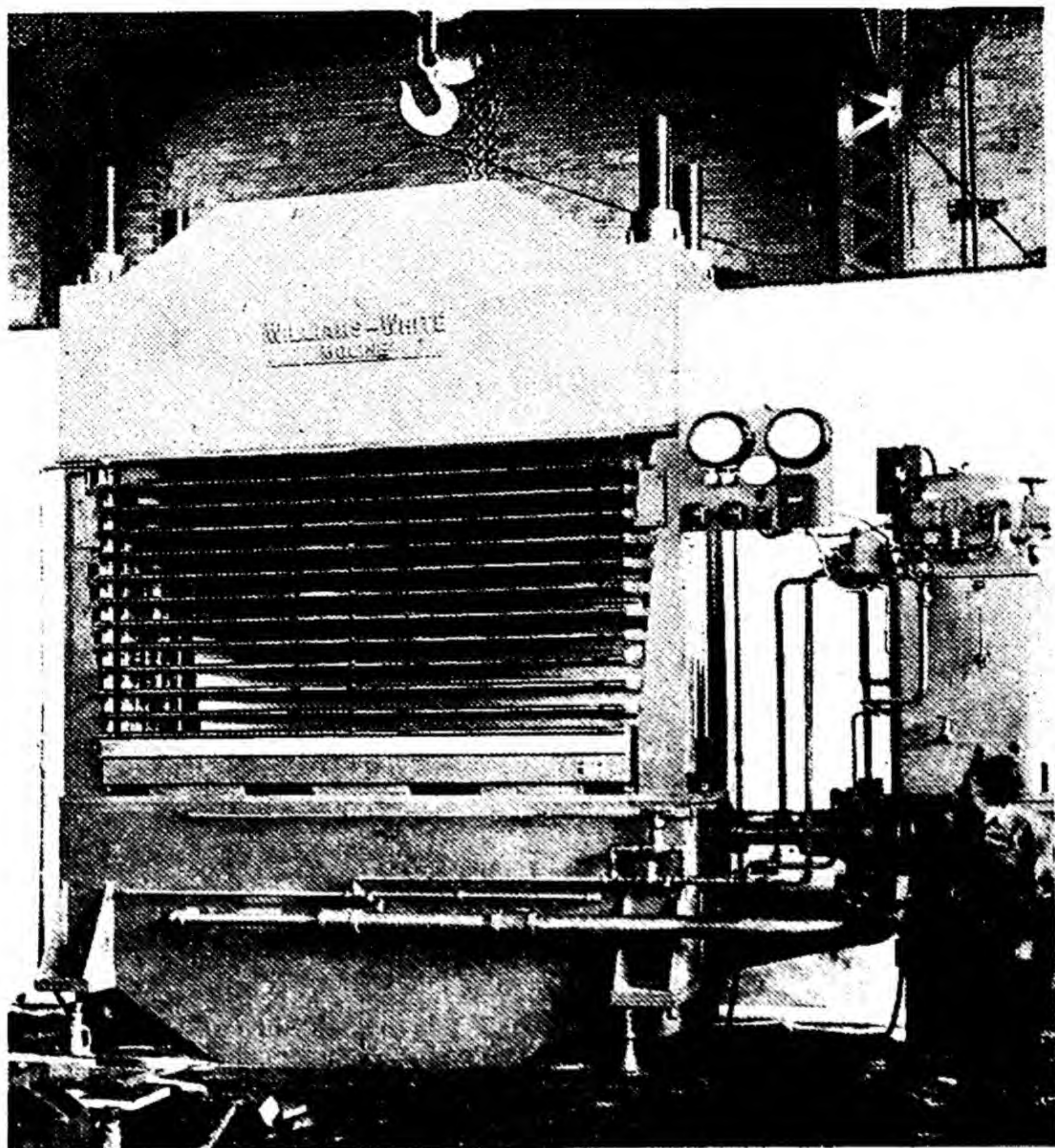

Fig. 35.—Large plywood press. (*The Resinous Products & Chemical Co.*)

formity and shorter heating cycles can be obtained. In addition, the supply of heat can be cut off immediately.

Plywoods can be surfaced with layers of materials other than wood. The various materials employed range all the way from paper to metals. This special surfacing produces a hard scratch-resistant surface with a low water-vapor penetration. Special permanent color or decorative patterns may also be produced by this method.

Plywood is an important material of construction. Its strength properties are superior to board lumber, yet it can be handled and fabricated just about as easily. It is widely used for airplane construction, boats, pre-

fabricated houses, furniture, and as a general wooden material of construction. The superior qualities of some of the newer adhesives have greatly broadened the fields in which plywood may be used, and plywoods are available with extremely high water resistance and excellent strength.

For the production of laminated shapes other than plywood, cloth or paper is continuously dipped into a pan containing resin dissolved in a solvent, run through squeeze rolls, and led into a drier, either vertical or
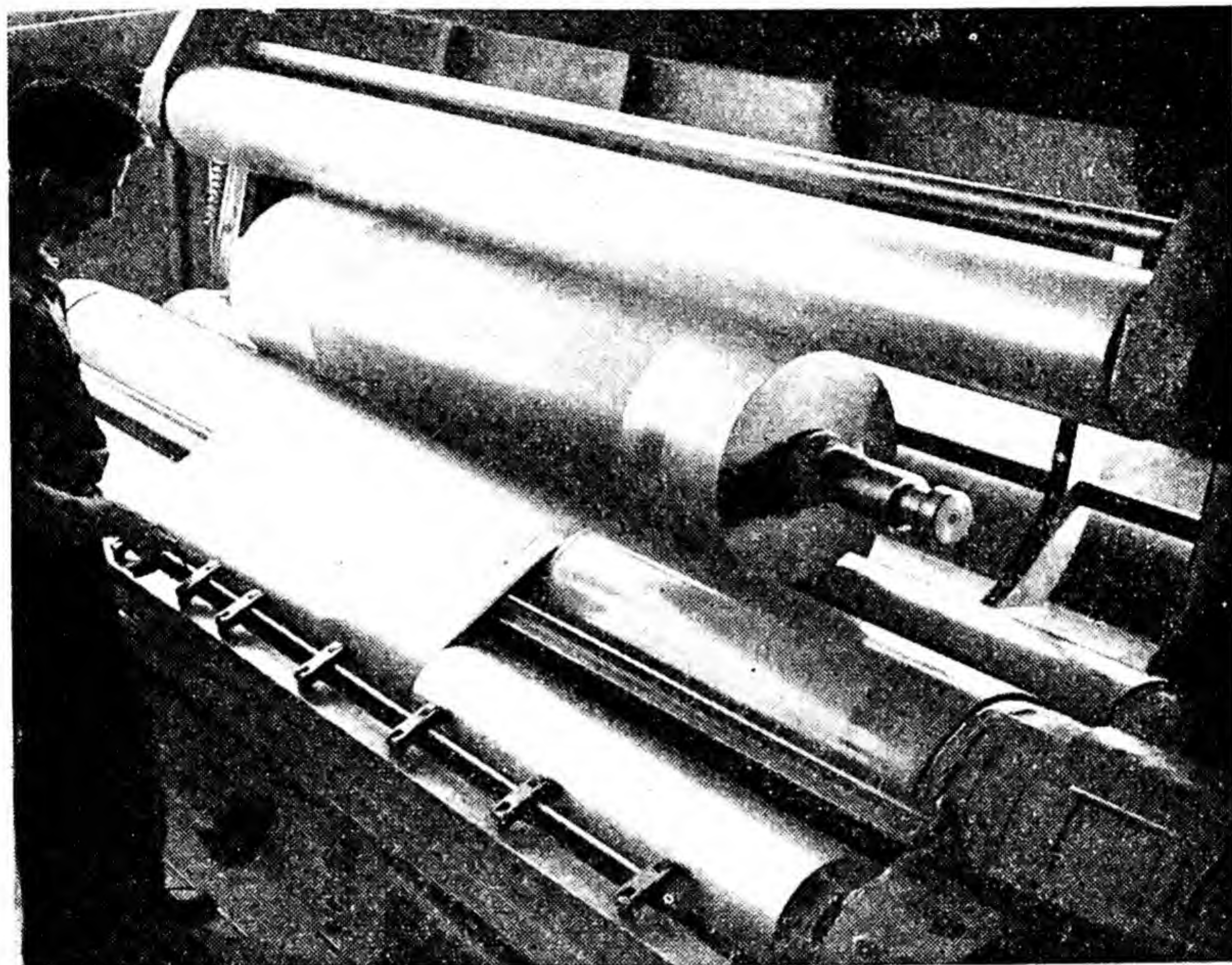

Fig. 36.—Rolling a large laminated tube. (*Synthane Corp.*)

horizontal, where the solvent is removed. It is then wound up and either used from the roll to make tubes and rods, or cut into lengths for pressing into sheets.

If sheets are to be made, individual sheets are piled up to the desired thickness and introduced into presses similar to those used for plywood. Polished-metal separators, or cauls, may be inserted between each assembly if a polished surface is desired. The assembly is placed between heated plates of the press and subjected to heat and pressure until curing is complete. Temperatures are about 300°F., pressures range from 1,000 to as high as 3,000 lb. per sq. in., and the curing cycle may be 30 min. to several hours.

Two types of tubes are made: molded and rolled. In both cases, the cloth or paper is rolled on a mandrel (see Fig. 36) having the correct inside

diameter, but the molded tube (see Fig. 37) is pressed between the two halves of a split mold, while the rolled tube is placed in an oven and baked for several hours. Each of these types has certain advantages for different applications. The manufacture of rods is the same as the procedure for making tubes, except that a small mandrel is used which is withdrawn before molding.

Phenol-formaldehyde or urea-formaldehyde resins are usually used as bonding agents. The phenolics have a characteristic dark amber color and
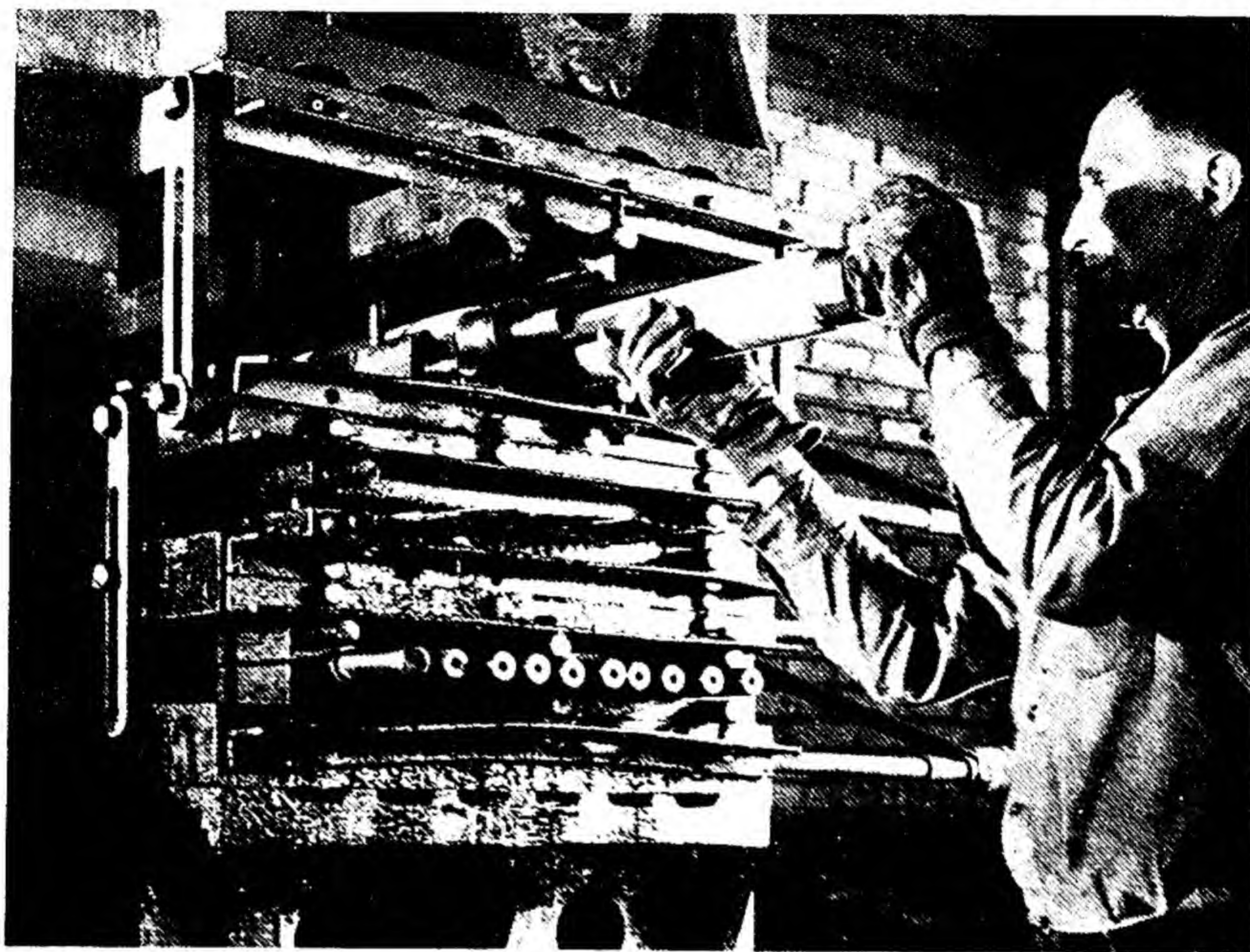

Fig. 37.—Molding laminated tubes.   (*Synthane Corp.*)

are used for the production of relatively dark colors. The ureas can be used for white or light pastel shades. In some cases, the surface sheets may be impregnated with urea resins, while the darker core is made with phenolics.

Special types of paper are used that have high absorptive power. Kraft paper is most generally used because of its low cost and satisfactory mechanical properties. Sulfite paper is used for applications requiring colorability, uniformity of appearance, and good electrial properties.

A variety of fabric bases may be used such as canvas, special ducks, twill, airplane cloth, or organdy. Weave and weight are important with regard to the strength, hardness, and density of the finished laminate. In general, the closer the weave of the fabric, the greater will be the tensile and impact strengths of the finished product.
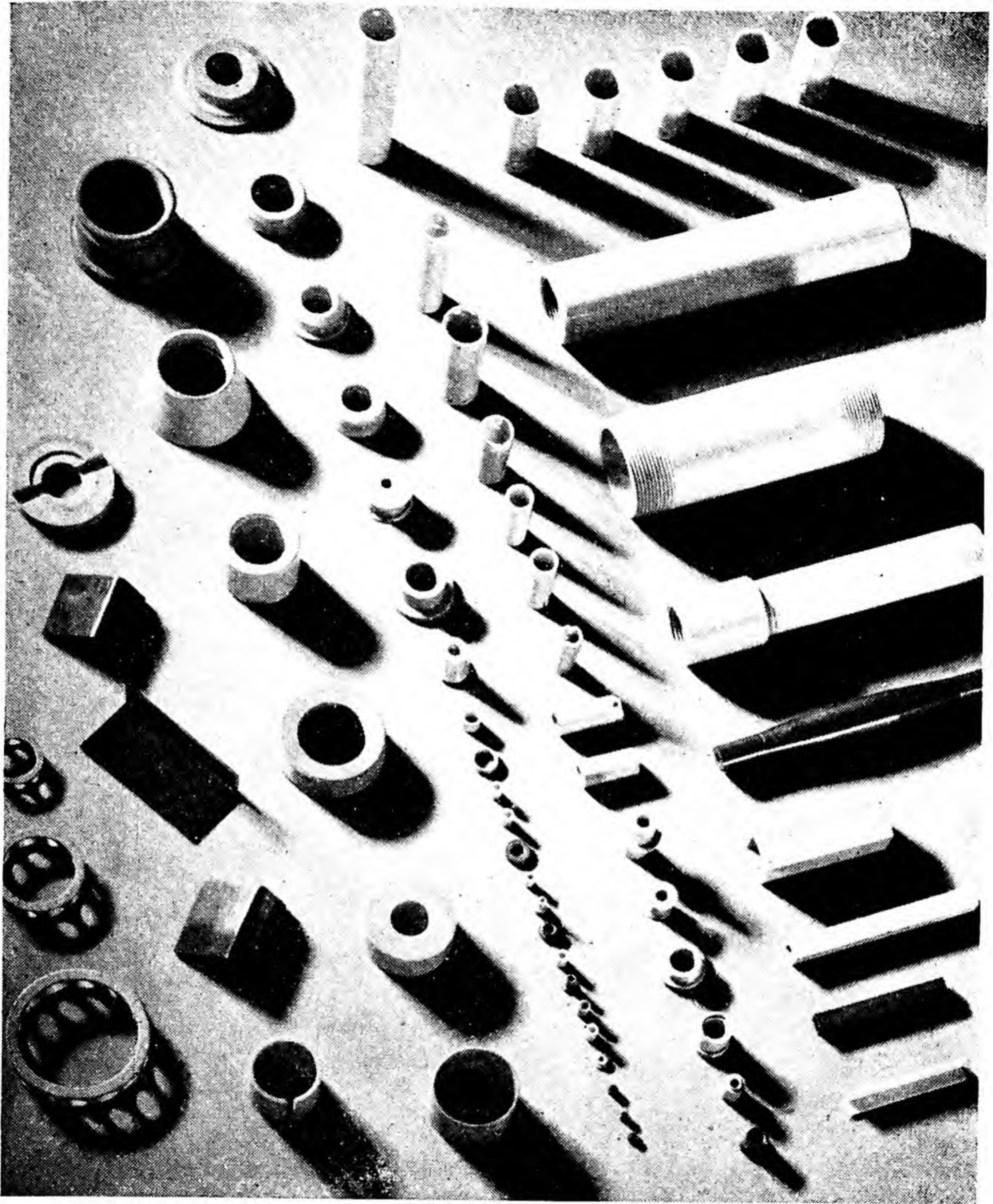
FIG. 38.—Various parts machined from laminated shapes. (*Synthane Corp.*)

Decorative sheets are produced for ornamental wall finishes, table tops, special cabinets, etc. The canvas-filled laminates are used for gears, cams, bearings, and special mechanical parts. Thin, easily fabricated sheets are used in the lighting and ignition systems of automobiles and airplanes. Switchboards are insulated with laminated punchings, and relays, cutoffs, control units, and induction coils make use of the high strength and good electrical properties of these high-pressure laminates.

The machining properties of these laminated sheets, rods, and tubes are excellent. In many cases it is cheaper to machine these stock shapes than to make a corresponding molded article. In addition, the laminated product has a much higher strength and impact resistance. A multitude of small punched or machined parts are produced for various industrial applications. Figure 38 shows a wide variety of products made from these laminates.

Blocking and Sheeting.—The blocking and sheeting process is described in detail in the discussion of cellulose nitrate. Essentially, it consists of properly plasticizing a plastic mass, pressing the mass into large blocks, and then shaving sheets from the block by a special knife. This process is confined to cellulose derivatives and maintains its importance because of the almost infinite variety of mixed colors and decorative effects that can be produced.

Built-up Structural Shapes.—In addition to the foregoing processes, which are commonly employed for the production of standard shapes, considerable experimental work has been done on built-up panels or sheets. In this construction, thin laminated sheets are separated by a core material in a sandwich construction. The core can be of extremely light material or can be a cellular structure since the main loads are carried by the outside sheets, which also act as a hard surfacing material. The great advantage of such panels is that they can combine large area with rigidity, or resistance to buckling, and extremely light weight. They also can be designed to provide excellent sound and heat insulation or vibration-damping properties.

An interesting panel of this type[1] is made up of a flexible, honeycomb, resin-impregnated glass cloth core between and bonded to thin laminations of glass cloth that form the skins, or surfaces, of the sandwich. The function of the core is to stabilize the skins of the sandwich so that they can develop a substantial portion of their ultimate compressive strength without buckling. The compression strength of the core normal to the faces must also be sufficient to resist local loads encountered in service. In building up these honeycomb cores, resin-impregnated glass cloth is passed between corrugated rollers to corrugate it. Piles of the corrugated cloth are laid upon one another and bonded to each other until a block is formed of the desired width. The block is then cut longitudinally to provide a core of the desired thickness, which resembles the appearance of an automobile radiator core.

This construction provides panels of extremely high strength and very low weight for structural members of aircraft, automobiles, etc. Built-up structures such as beams have also been produced.

[1] SLAYTER, G., and H. W. COLLINS, paper presented at the December, 1945, meeting of the American Institute of Chemical Engineers, Chicago, Ill.

Plastic Foams.—Extremely lightweight cellular structural materials are produced by making "solid" foams from various resins (see Fig. 39). Two general methods of making foams are in use. In one, a solid that will liberate a gas on heating is incorporated in a resin and the foam is produced by heating. In the other, foams are produced in liquid monomers or partly polymerized resins and the final polymerization sets the foam. In either case, the foam must be solidified by hardening the cell walls by cooling, polymerization, or vulcanization.
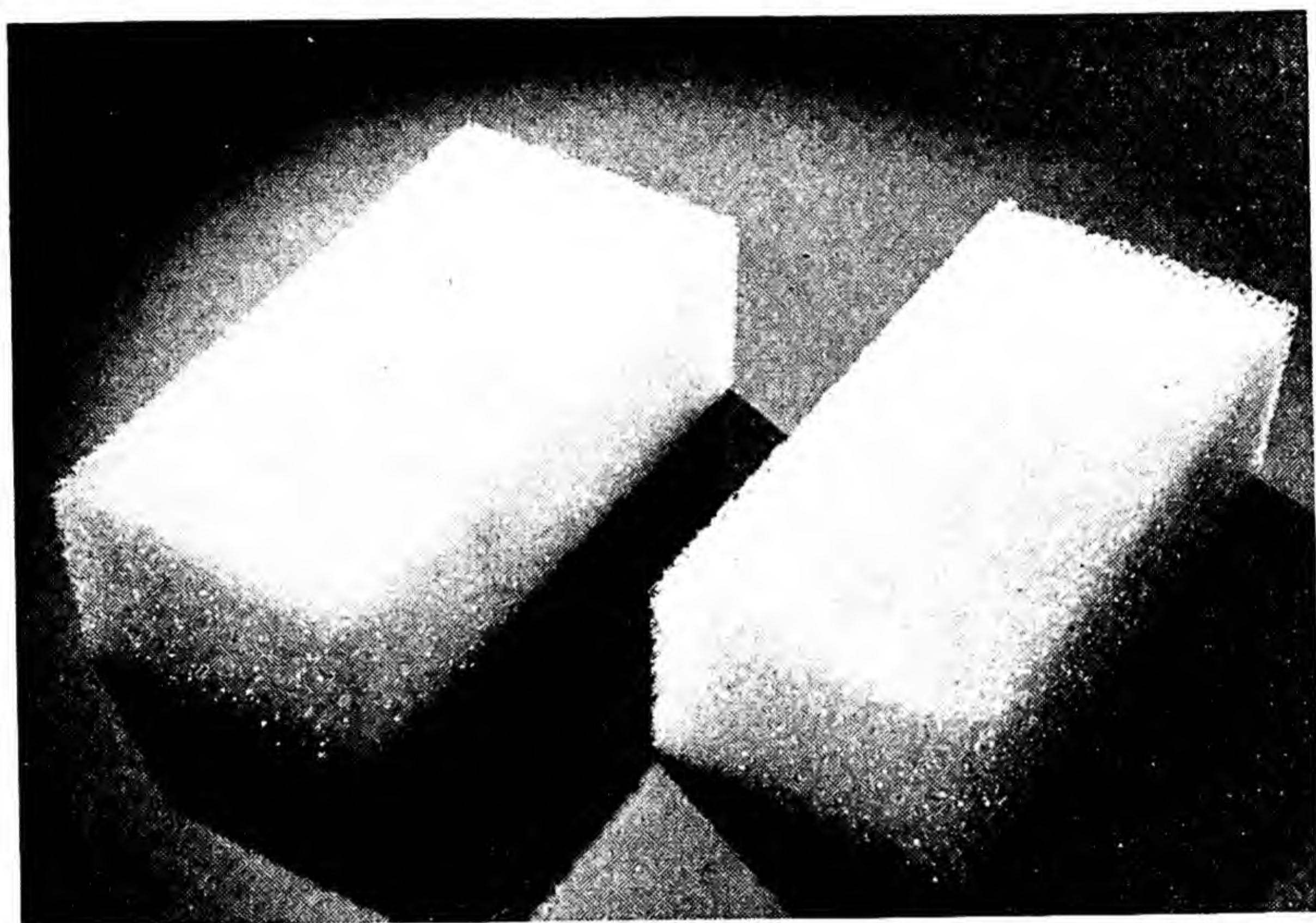

Fig. 39.—Blocks of polystyrene foam having a density of less than 2 lb. per cu. ft. (*The Dow Chemical Co.*)

The formation of cellular plastics by the use of carbonates is similar to the rising of bread. Carbonates are carefully dispersed in the solid thermoplastic resin by mixing and milling. Usually some moisture as well as a weak organic acid is also incorporated. The actual expansion into a foam is accomplished when the mixture is heated, releasing carbon dioxide and blowing the semifluid resin into a foam. The heating is done either in a mold, which is released before cooling to allow the expansion to take place, or in an extruder, which shapes the foam as it emerges and then hardens it by cooling on an endless belt. Sheet stock is also made by electronic heating of sheet material between electrodes, which expand as the foam rises.

The production of plastic foams from liquids is not as adaptable to the production of desired shapes, since a foam mass is produced that must be cut up to produce block shapes, with a resulting high cost due to the labor and wastage. These methods establish the foam by whipping air into the

liquid or by means of gas generated in the liquid. When air is used, it is whipped into a hot viscous liquid that is partly polymerized, and the final polymerization solidifies the foam before it can collapse. The other process incorporates chemicals in the polymerization reaction mass which react to liberate large quantities of carbon dioxide or other gases. They are added at a point where the reaction mass has become homogeneous and the polymerization will proceed smoothly and rapidly to give the desired polymer. In effect, this process merely transforms the whole liquid reaction mass into a foam, and the reaction is concluded in the foam phase. These foams require drying since water is present or is liberated by the polymerization. A variation of this process employs foaming agents and stabilizers to produce a foam of the monomer, which then polymerizes by the application of heat.

Foamed materials have been produced from almost all the resins, including phenol- and urea-formaldehyde, polyvinyl chloride, polystyrene, rubber, and cellulose acetate. The chief uses for these products have been for insulation and as floatation aids for life rafts and jackets. Their cellular construction gives them a very low thermal conductivity and makes them poor transmitters of sound. They show great promise as a cheap, readily fabricated filler for the sandwich-type built-up structural shapes previously mentioned. For this purpose, the outer sheets that make up the sandwich need not be a plastic material, but can be aluminum or other metals. These strong, extremely light structures are very important wherever a high strength-weight ratio is desired. The use of rubber foams for upholstering and mattresses has produced high-quality products in these fields for several years.

ADHESIVES

Vegetable mucilages and animal glues were used as adhesives since the beginning of history and played an important part in the fabrication of many articles. They were, and are, capable of supplying a good bond under dry conditions but failed if the joints became damp. In addition, they could be used only on certain materials such as wood and paper. The introduction of casein and blood glues achieved a marked improvement over animal glues with respect to water resistance. However, these protein materials are also subject to fungus attack and are not completely water-resistant; certainly they are not waterproof. The advent of synthetic resin adhesives has caused a tremendous improvement in this field. It is now possible to bond materials with adhesives that are so tenacious that in many instances the bond is stronger than the cemented materials. Even with metal-to-metal bonds, the strength of the bond is of the same order as the strength of the weaker metals themselves. Evidence of this fact is the adhesive bonding of many airplane structural parts.

Some of the synthetic resin adhesives are completely waterproof and will even resist chemical attack. But it is not one single property that makes these newer adhesives important, rather it is their versatility. Most of the numerous synthetic resins have adhesive powers of varying degrees, and their properties in this respect can be greatly altered by varying the method of production, formulation, and application. Recently, the trend has been toward the development of specific adhesives for specific purposes with a great deal of attention being paid to surface preparation as well as the special coating of surfaces with resins to form a base for the adhesive. Special methods of application have also been developed for specific materials, until it is now possible to use this method of joining most of the common materials from fabrics to stoneware.

The use of the various resins as adhesives is so varied that applications of specific resins will be discussed under the particular resin involved. However, some of the more generalized factors of importance in this field can be summarized.

Resins to be used as adhesives may be in the liquid state, in solution, as a paste, a powder, or a film or tape either in sheet form or impregnated paper or cloth. The use of films and tapes has been of tremendous importance in speeding up and improving the quality of application. Brushing, spraying, rolling, and dipping methods are all used with the other forms of adhesives. In contrast to the older glues, some of the newer adhesives permit much longer periods of time between application to the surface and final assembly of the joint. This makes it possible to put complicated assemblies into special jigs, clamps, and presses, where an appreciable time is required for complicated or irregular structures.

The fact that some resins are thermoplastic while others are thermosetting is important both as regards methods of application and the properties of the finished joint. If thermoplastic resins are applied in solution; temperature, time, and porosity conditions in the press need only be such that the solvent can be driven off without disturbing the bond. If this type of adhesive is used as a film, or if the two surfaces are previously coated and then pressed together, temperatures must be high enough to cause the resin to soften or become tacky so that it will seal under pressure. Thermoplastic resins cannot be used as adhesives if temperatures encountered in service are high enough to cause softening.

Thermosetting resins may be applied by all the methods previously mentioned. In general, they are applied in a partly polymerized state and must be cured while the joint is under pressure. If the shapes are such that they can easily be hot-pressed or will withstand temperatures of 200 to 300°F., heat is usually applied to aid in the final curing, particularly with phenolic types. However, special resins and catalysts have been developed so that it is possible to complete the cure at room temperature

in a reasonable length of time, a feature that is extremely important to the small manufacturer who may not produce enough pieces to warrant the installation of relatively large ovens with the required expensive controls. Thermosetting resins produce the most impervious adhesives. Joints can be completely waterproof, resist high temperatures, and are not attacked by fungi. The use of plywood construction on boats and airplanes is a good example of the durability and strength of this type of adhesive.

Fig. 40.—An adhesive whose bonding power is due to tackiness. (*Minnesota Mining & Manufacturing Co.*)

Adhesives possessing rubberlike properties form another important class. This type may be applied in solution or in the form of films and tapes. If used in solution, the same considerations are of importance as was the case for thermoplastic resins, except that some additional curing may take place with the application of heat. Tapes and films may owe their adhesive properties merely to their tackiness (see Fig. 40), or they may be tacky when applied and be cured by heating. This type of adhesive may be compounded from one or more of the rubbers, a specially prepared thermoplastic with rubberlike properties, or a mixture of a rubber with other resins.

The importance of adhesives is increasing rapidly. Methods of fabri-

cating almost all materials have been profoundly influenced, and indications point toward even greater developments. The use of adhesives in the low-pressure molding of such objects as boat hulls and airplane wings is a good example of new methods of fabrication, and the replacement of riveted, bolted, screwed, and nailed joints with an adhesive bond indicates the possibilities of bonding as a method of fabrication. Adhesive bonding is so varied in its application that all phases cannot be taken up here, but it should be realized that in all its forms it is the most generally used method of joining materials.

FIBERS, FILAMENTS, AND FOILS

The development of synthetic fibers as substitutes and to augment natural products represents a brilliant achievement by research workers and engineers. Rayon was first manufactured on a commercial basis in the United States in 1911, starting an American industry that is now valued at over 500 million dollars. The first year's production was less than 400,000 lb. as compared with the 1945 production of 790 million pounds. The industry still is growing steadily, as indicated by the following statistics:

Table 2.—UNITED STATES RAYON PRODUCTION*

(Units are millions of pounds)

	1945	1944	1943	1942	1941	1940
Filament yarn	624	555	501	479	451	390
Staple fiber	168	169	162	153	122	81
Total	792	724	663	632	573	471

* *Rayon Organon*, February, 1946.

The term "rayon" includes viscose, cuprammonium, and acetate types. In 1945, the production of viscose and cuprammonium rayon was 580 million pounds and the newer acetate type amounted to 212 million pounds. There is only one plant producing cuprammonium in the United States, and it amounts to less than 2 per cent of the total. The manufacture of cellulose nitrate rayon was discontinued in the United States in 1934.

In spite of the rapid growth of the rayon industry, it represented only about 11 per cent of the fibers used in the manufacture of textiles in the United States, as the following figures show:

TEXTILE FIBER CONSUMPTION IN 1944

	Pounds
Rayon	705,000,000
Wool	624,000,000
Cotton	4,787,000,000
Total	6,116,000,000

Figure 41 indicates the remarkable growth of rayon manufacture in the past 24 years and Table 3 lists manufacturers, processes employed, and trade names.

TABLE 3.—MANUFACTURERS OF RAYON IN THE UNITED STATES*

Viscose Process	Trade Names
American Enka Corp.	Perglo, Briglo, Englo, Tempra (high tenacity), Vitala (high tenacity)
American Viscose Corp.	Crown, Dulesco, Chalkelle, Tenasco (high tenacity), Fibro (staple fiber), Avisco (high tenacity stable fiber)
Delaware Rayon Corp.	Delray
E. I. du Pont de Nemours and Co.	DuPont Rayon, Cordura (high tenacity)
Hartford Rayon Corp.	Hartford
Industrial Rayon Corp.	Spun Lo, Premier, Dul-tone, Spun-black, Tyron (high tenacity)
National Rayon Corp.	National
New Bedford Rayon Corp.	Newbrary, Newlow, Newdull
North American Rayon Corp.	North American, Xtra-dull, Supernarco (high tenacity), High Narco (high tenacity)
Skenandoa Rayon Corp.	Skenandoa
Tubize-Chatillon Corp.	Tubize, Chardonize, Hygram (high tenacity)
Cuprammonium Process	
American Bemberg Corp.	Bemberg, Matesa, Aristocrat, Star Breeze, Snowkrepe
Acetate Process	
American Viscose Corp.	Seraceta, Seraceta Fibro (high tenacity)
Celanese Corp. of American	Celanese, Fortisan (saponified), Celairese (staple fiber)
E. I. du Pont de Nemours and Co.	Acele
Tennessee Eastman Corp.	Eastman, Koda, Teca (staple fiber)
Tubize-Chatillon Corp.	Chacelon

* From *Textile World*, September, 1943.

In addition to the rayons, several other synthetic fibers have been produced on a commercial or semicommercial scale. With the exception of glass fibers, all of them are produced from synthetic resins. Some are intended for general use as a textile material, others are specialty products to be used where severe conditions warrant a better and more expensive product. In addition to fibers, monofilaments are important in this group of resins. The difference is only one of size as far as the product is concerned. Bristles, racket strings, and the like are designated as monofilaments. Table 4 lists the various synthetic fibers other than rayons now in production in the United States.

Of the fibers other than rayon, nylon is by far the most important. It approaches silk more nearly than any other synthetic fiber, and in some of
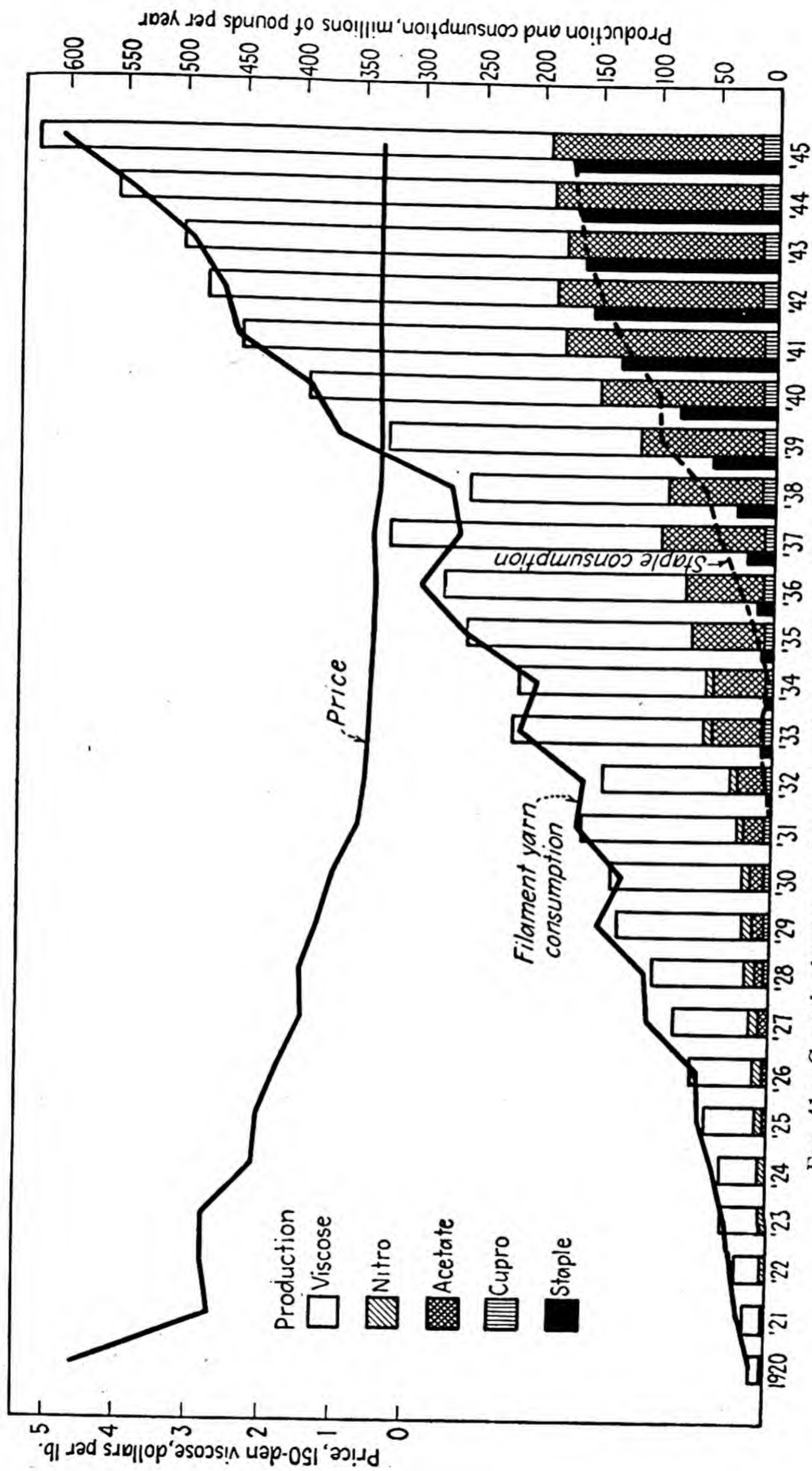
Fig. 41.—Growth of rayon production for the period 1920–1945. (*Chem. and Met.*)

its properties it is superior. Present production is nearing 30 million pounds per year, and additional capacity is planned. Although nylon was used primarily for women's hosiery, and this field probably will provide the largest single outlet, other important uses have been developed. Nylon rope, bristles, and fabric are all of high quality and in great demand for both military and peacetime applications.
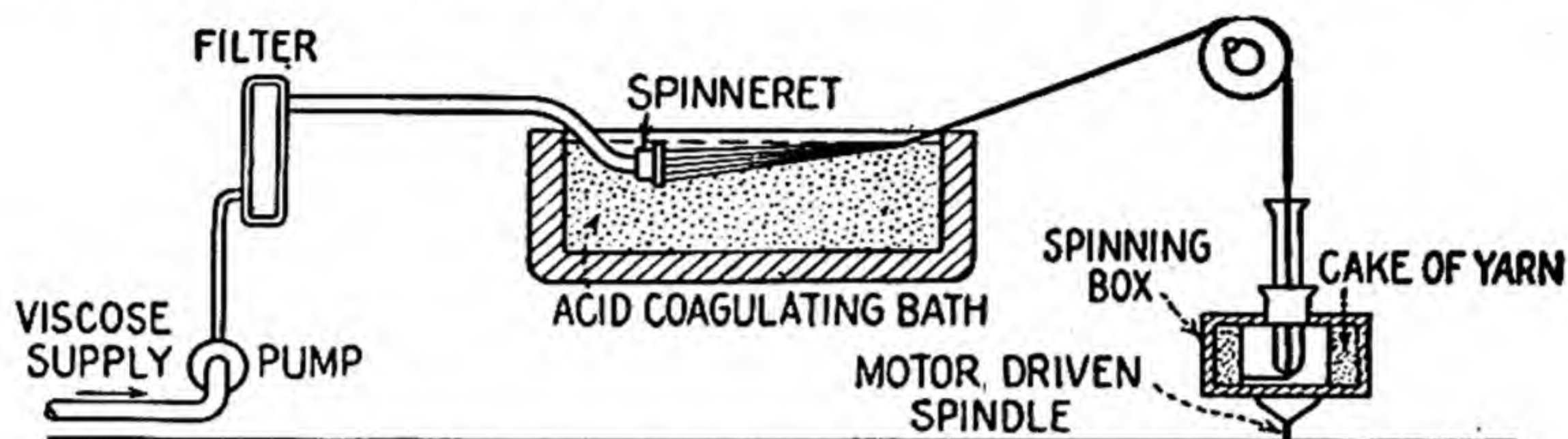
FILTER

SPINNERET

SPINNING BOX

CAKE OF YARN

VISCOSE SUPPLY   PUMP

ACID COAGULATING BATH

MOTOR DRIVEN SPINDLE

Fig. 42.—Viscose-rayon spinning operation. [*Chem. Eng. News*, **22**, 1989 (1944).]

Aralac, a fiber produced from milk casein, is next in order of quantity produced, production being over 8 million pounds a year. These protein fibers resemble wool chemically as well as physically and at present are used in blends with wool or in replacing wool in blends with other materials.

Most of the other synthetic resin fibers have special applications depending on their specific properties and will be discussed under the particular resin used to produce them.

Fiber Formation.—There are three basic processes for the formation of fibers. All of them involve extruding a viscous liquid or "dope" through spinnerettes which are essentially extrusion dies containing 1 to 60 very small holes. The differences in the processes lie in the method of solidifying the liquid resin after it emerges from the spinnerette. In one process, the molten polymer is hardened by cooling; in the second process, a solution is extruded and the solvent vaporized by warm air or flue gas; the third class involves a chemical reaction that coagulates the liquid by means of the proper chemical solution as it leaves a spinnerette submerged under the solution (see Fig. 42 for a typical example).

Yarns are identified in the trade by the number of filaments and denier, the latter is the weight in grams of 9,000 m. of the yarn. The smaller denier or finer yarns bring a premium in price.

All the basic processes require processing of the fibers after spinning. As might be expected, the molten and solution methods require considerably less treatment than the coagulation processes. The detailed description of the various processes is included under the specific resin involved. Recent developments include continuous processing methods, which should greatly reduce the cost.

Although the basic steps involved in spinning synthetic fibers may be

relatively simple, the actual operation requires extremely close control in the preparation and use of the dopes, and the mechanical operations of the pumps and the bobbins must be precise. In addition, skilled operators and maintenance men are required.

TABLE 4.—PRODUCERS OF SYNTHETIC FIBERS IN THE UNITED STATES *

Basic material	Trade name	Producer
Nylon..................	Nylon (generic)	E. I. du Pont de Nemours and Co.
Vinyl polymer...........	Vinyon, Vinyon E.	American Viscose Corp.
Vinylidene polymer.......	Saran	Dow Chemical Co.
	Velon	Firestone Industrial Products Co.
	Permalon	Pierce Plastics, Inc.
Milk casein..............	Aralac	Aralac, Inc. (division of National Dairy Products Co.)
Glass..................	Fiberglas	Owens-Corning Fiberglas Corp.
Synthetic rubber yarns.....	Ameripol	B. F. Goodrich Co.
		U. S. Rubber Co.
Plastic-coated yarns.......	Plexon	Freyberg Bros.-Strauss, Inc.
Polyethylene.............	Polythene	Carbide and Carbon Chemicals Corp.
		E. I. du Pont de Nemours and Co.
Styrene.................	Polyfibre	Dow Chemical Co.
Cellulose acetate-butyrate..		Erie Resistor Co.
		Pierce Plastics, Inc.
		The Rex Co.
Ethyl cellulose...........	Ethoraon	Dow Chemical Co.
Soybean protein..........	Soylon	The Drackett Co.
Corn-meal zein...........		Corn Products Refining Co.

* From *Chem. & Met. Eng.*, **52**, 126, (1945).

Rayon is manufactured as a continuous-filament yarn and as staple fiber. The latter is cut in lengths of $1\frac{1}{2}$ to 8 in. and is spun much the same as cotton into a fiber resembling wool. Its use is expected to increase rapidly.

Foils.—The manufacture of foils and thin sheets is discussed under viscose. This material is made into cellophane in very large tonnage and is used extensively for wrapping purposes. A similar product is made from cellulose acetate and cellulose acetate-butyrate on roll-coating machines from dopes. Thicker sheets are made by extrusion of the molten material through slits.

In Germany during the war, films of nylon, cellulose acetate-butyrate,

and cellulose triacetate were made on band-casting machines in thicknesses of 0.05 to 0.2 mm.

IMPREGNATING AGENTS

The total tonnage of resins used for impregnating materials is small in comparison with the other main applications, but it is an important use since the entire character of some materials may be altered by impregnating them with synthetic resins. In many cases, the fact that the entire body of the material is altered in character, rather than just the surface, is the best way to distinguish between impregnation, coating, and the application of adhesives. It is certainly true that many coatings and adhesives penetrate into the material to which they are applied, but their primary purpose is to alter or bind the surface only.

Perhaps the best example of an impregnating agent that completely alters the character of the material is the impregnation of wood with methylol urea, the monomeric unit of urea-formaldehyde resins, and then carrying out the polymerization reaction in the cells of the wood. The product has completely altered properties. It will not swell, shrink, or warp with humidity changes, and the grain will not rise on wetting. Soft woods that have not been used as a material of construction because of their softness can be hardened until they can be worked, turned, and finished to give a product that is superior to the hardwoods. This type of impregnated wood gives promise of becoming another material of construction.

Phenolic resins are used to impregnate veneers, which are then bonded to the other layers of plywood to produce an altered surface. In this use they can be regarded as impregnating agents since the veneer has an appreciable thickness. Paper is also impregnated for this use. In the making of paper and cloth laminates, phenolics are used to impregnate the sheets before bonding. In this case, the resin serves both as an adhesive and as an impregnating agent.

Melamine and urea resins have found a very important role in the development of papers with excellent wet-strength characteristics. A considerable quantity of these resins is being used to impregnate paper to improve its wet strength.

Resins are used as impregnating materials in the textile industry for many purposes. The development of starchless collars and cuffs was made possible by the use of resins. They are now being developed for the production of wrinkleproof fabrics for clothing. They are used for sizes or finishes in the production of natural yarns and rayon. A recent development is the use of melamine resins to impregnate cotton and wool products to make them completely shrinkproof without preshrinking.

There are many applications in this field that are not in use at the present time. In many cases this is due to the belief that the added expense is not warranted or that the improvement in quality is not necessary. Certainly improvement in quality is one of the contributions of impregnating agents in every case, and we can look forward to numerous new applications now in the process of laboratory development.

PART III

RESINS FORMED FROM HIGH MOLECULAR-WEIGHT NATURAL PRODUCTS

The resins in this class have as their source high molecular-weight products produced by growing plants, insects, animal or vegetable proteins, or polymerized gums produced by long aging during the fossilization of plant materials. · They include the oldest types of resins known, which were, and are still, obtained merely by purifying and using existing resins formed by nature. They also include resins produced by chemically altering high polymers that have already been polymerized by natural processes. In this respect, they are not synthetic materials, since the processing employed to produce finished resins is done only to alter their properties and not to synthesize the basic high molecular weight structure.

In the case of the natural products that have important uses without chemical alterations, the processing necessary to produce finished resins usually only requires physical methods of purification to improve color and clarity and to remove the more volatile materials that are frequently present. The chemical alteration of natural high polymers, on the other hand, produces marked changes in their properties and, in many cases produces a material that does not resemble the basic raw material. In this respect a new and useful material has been obtained through chemical reactions, and the final product is in reality synthesized from an existing raw material.

Until the later part of the nineteenth century, the unaltered natural products were the only source of resinous materials and the classical concept and definition of a resin was based on them. During the 1870's, cellulose nitrate began to appear on the market under the familiar trade name Celluloid. This marked the start of the tremendous expansion of the use of high polymers to its present position in industry.

Fossil and Plant Resins.—(Excluding Rosin).—Natural resins are exudations of trees of many different species. These secretions or exudations may be those of living trees or may be fossilized products. They have been known and used for coatings, etc., from very early times. They were used by the Egyptians to varnish their mummy cases and are still extensively used as varnish and ink resins, in waxes, and in cements and adhesives.

These resins are divided from point of use into two solubility classes: the so-called "spirit-soluble" and the oil-soluble types. Originally the term

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spirit referred to alcohol, but it now refers to a general class of solvents. This type of resin is directly soluble without processing. The oil-soluble type must be thermally processed before it will dissolve in the various oils used in varnish making. In general, the spirit-soluble type is the softer variety, but almost any degree of hardness and solubility may be obtained in the complete range of the various natural resins.

Natural resins can be classified as follows:[1]

1. Dammars
   a. Batavia (Sumatra, Borneo, Java, East Indies)
   b. Singapore (Malay States)
      Directly oil-soluble. Used in conjunction with synthetic resins, in inks, rapid-drying varnishes and wax.
2. East Indies
   a. Batu (Malaya, East Indies)
      Related to dammars but gives more viscous solutions. Good for cements, gaskets, etc.
   b. Black (Malaya, East Indies)
      Similar to dammars. Dark colored but bleaches to transparent film. Good resistance to alkalies.
   c. Pale east india singapore (rasak) and macassar (Sumatra, Borneo, Malaya, East Indies)
      Similar to dammars. Compatible with most resins and solvents. Widely used.
3. Copals
   a. Manila (Netherlands East Indies, Philippine Islands)
      Several types. Used in varnishes, lacquers, paints, etc. Processed by heating to make them oil-soluble.
   b. Congo (Belgian Congo)
      Insoluble in most organic solvents in crude state. Must be thermally processed. Variety of uses from cellulose nitrate lacquers to special varnishes. Excellent adherence to metals.
   c. Kauri (New Zealand)
      Soluble in alcohols and ketones but usually processed. Used in a wide variety of varnishes, lacquers, etc.
4. Miscellaneous resins
   a. Aceroides (Australia)
      Thermosetting. Used for paper coating, spirit varnishes, inks.
   b. Elemi (Philippines)
      Used as a plasticizer and in combination with synthetic resins in varnishes.
   c. Mastic (Island of Chios, Greece)
      Used for special varnishes to protect paintings, etc.
   d. Sandarac (Africa and Australia)
   For a hard, white spirit varnish.

Rosin.—The recovery of oils and gums from the oleoresin of the pine tree is an ancient art. Pliny and Herodotus mention the recovery of turpentine from pine trees. The first record of distillation of an essential oil

[1] MANTELL, C. L., C. W. KOPF, J. L. CURTIS, and E. M. ROGERS, "Technology of Natural Resins," John Wiley & Sons, Inc., New York, 1942.

was for turpentine.   One of the reasons for sending the first English colony to Virginia was to obtain a source of pine pitch and other naval stores.

The term "naval stores," now refers only to rosin, turpentine, and pine oil, but originally it also included lumber, masts, sails, and rope.   Turpentine, tar, and pitch were produced in this country as early as 1608, and the industry was firmly established in North Carolina in the early part of the eighteenth century.   After 1880, the industry moved farther south into Georgia and Florida.

Rosin is obtained from southern pine trees either by tapping the trees or by extracting the rosin from pine stumps.   It consists chiefly of the rosin acids, of which abietic acid is the most important.
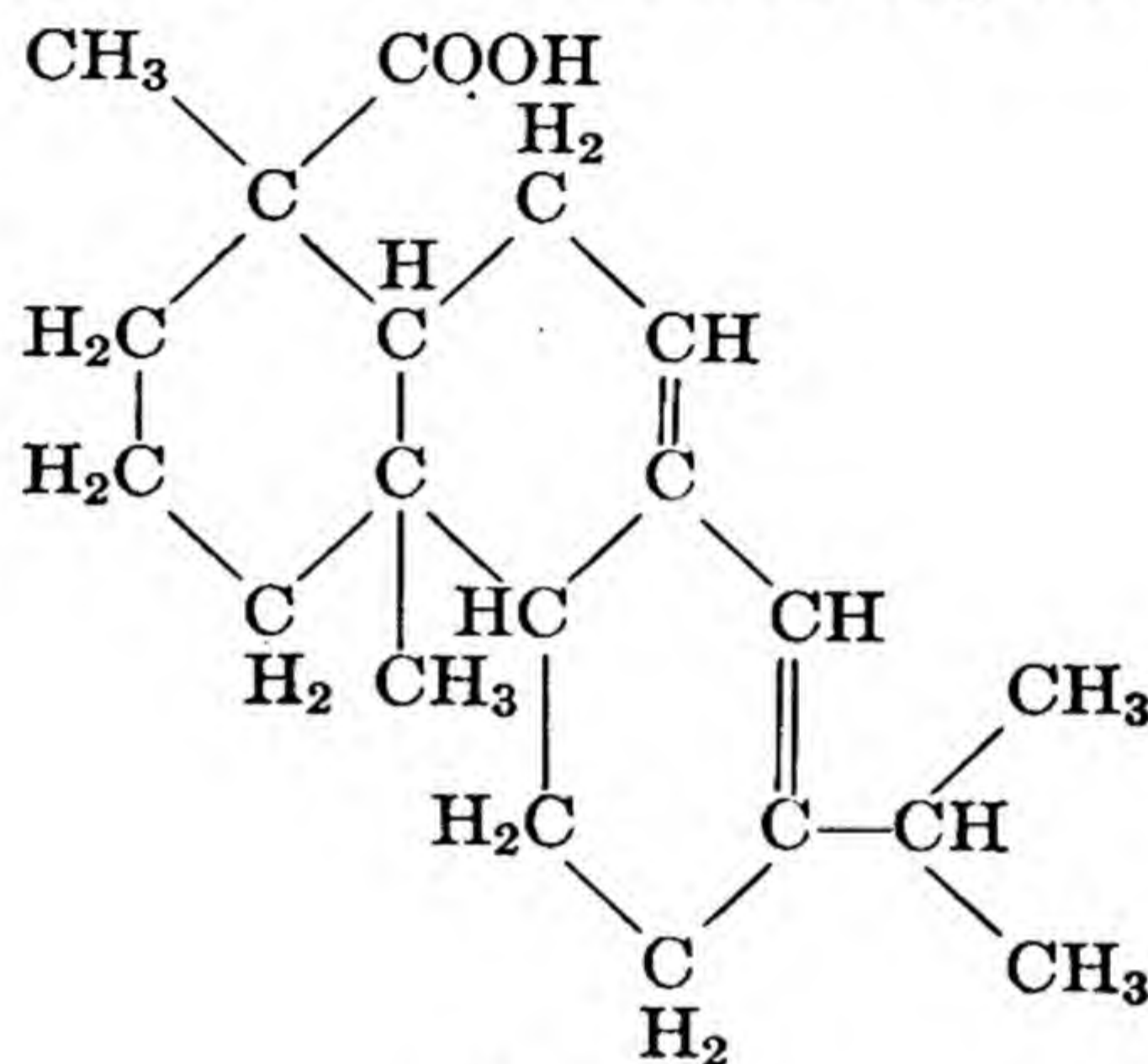
Abietic acid

The three large consuming industries for rosin are paint and varnish, soap, and paper.   Rosin is used directly as a resin in paint and varnish manufacture, usually in conjunction with synthetic resins, or it may be made into various esters and then incorporated.   The largest single use is as a paper size.   Large quantities also go into the manufacture of rosin soaps and greases.

Rosin is collected by tapping pine trees in the southern part of the United States from April to November.   A cup and gutters are attached to the tree, and a groove or streak is cut just above the gutters.   A fresh streak is cut every week while the gum flows.   As the oleoresin exudes, it flows down the tree into the gutters and then into the cup.   The gum contains about 68 per cent rosin, 20 per cent turpentine, and 12 per cent water and is collected every 3 or 4 weeks and steam distilled.

The turpentine obtained from the initial steam distillation is ready for shipment without further refining.   The rosin is nonvolatile and is left in the still.   It usually contains bark, twigs, pine needles, and other foreign matter, removed by skimming from the top or by running the hot rosin

through screens and cotton batting. The rosin is then dipped into barrels and drums for shipment.

In another process, rosin is obtained by extraction from the wood of old pine stumps. Large acreages are cleared of stumps annually, but there seems to be a plentiful supply for many years to come. Most of the stumps have been in the ground 10 to 15 years. This length of time is preferable, as the resin content increases with age.
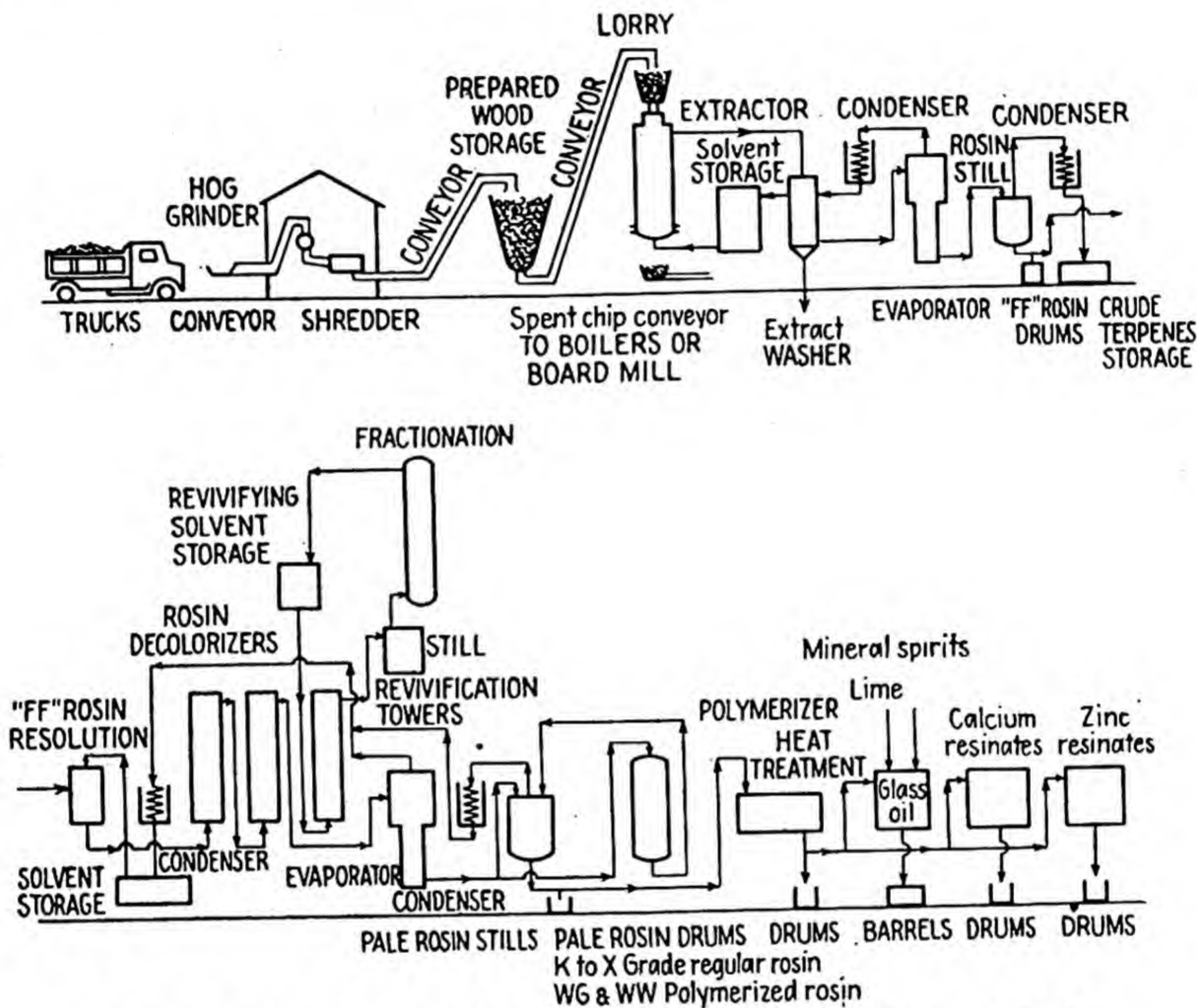

FIG. 43.—Flow sheet for the production of rosin. (*Chem. and Met.*)

A single plant may use as much as 1,300 tons of stump wood daily. The wood is brought in by wagon, trucks, and freight cars and may be carried up to 100 miles. The wood is first ground by passing it through a hog and then shredding it to pieces varying up to 1½ in. in length. The ground wood is conveyed to retorts in which the turpentine and rosin are extracted by a volatile solvent. A low-boiling solvent is used which can readily be separated from the turpentine by distillation. The extracted wood is steamed to recover the solvent (see Fig. 43).

The turpentine, pine oil, and rosin are dissolved in the solvent, which is removed by evaporation. Turpentine, dipentene, and pine oil are distilled off and fractionated to produce a variety of grades of these solvents.

The rosin obtained by this method is ruby red in color and contains

about 25 per cent oxidized rosin.   This FF rosin was for years the only rosin produced from pine wood, but at the present time there are some 40 different rosins, differing from each other either as to color or in some type of special treatment.

Many solvents are capable of removing the coloring matter from rosin. In the solvent-extraction method of decolorization, the rosin is first dissolved in a petroleum naphtha, which is a relatively poor solvent for the color bodies.   A selective solvent is then added that is relatively insoluble in the naphtha but is an excellent solvent for color bodies.

Furfural has been found to be the most satisfactory selective solvent. It is added to the naphtha solution of rosin and the temperature raised to about 125°F. to bring about complete miscibility.   On cooling, a furfural layer containing the dark-colored materials separates out.   The two layers are separated, and the furfural is recovered by steam stripping. This process is similar to the solvent extraction of a heavy lubricating oil.

By varying the ratio of furfural to rosin, the temperature, and the time of contact, the extent of decolorization can be varied to produce a wide variety of color grades from very pale to relatively dark.

The other process for removing color from rosin resembles the clay percolation method for decolorizing lubricating oils.   Filter clays such as fuller's earth or synthetic magnesium silicate are used to absorb the color bodies.

The dark (FF) rosin is dissolved in a petroleum naphtha to about a 10 per cent solution and washed with water, which removes a small amount of the dark rosin.   The naphtha solution is then pumped through several large towers filled with the clay.   The clay at first absorbs all the rosin, but, as more solution passes over the clay, the darker rosin is preferentially adsorbed and the lighter colored unoxidized rosin passes through.   The rosin solution is then displaced with fresh naphtha, and the naphtha is stripped from the product by steam in aluminum stills.

Since the amount of clay used is approximately two and one-half times the weight of the rosin, it must be reactivated and used over and over. It is reactivated by washing with a mixture of alcohol and naphtha.   This solution gives a residue of dark-colored oxidized rosin on evaporation. The alcohol left on the clay is removed by hot naphtha, and the clay is ready for use again.

Natural wood rosin as produced by these processes, if dissolved in alcohol, linseed oil, or mineral thinner, will tend to crystallize out of solution on standing, a serious disadvantage in varnishes and printing inks.   It was found that a heat-treatment at 265 to 285°C. for 2 to 2½ hr. brings about important changes in the rosin that reduce the tendency to crystallize. A certain amount of decarboxylation and isomerization occurs which yields a permanently soluble rosin.   Various grades of heat-treated rosins are

available that are definitely superior to natural rosins for use in varnishes and inks.

As an alternative to heat-treatment, rosin can be made permanently soluble in oils, but not in alcohol, by the incorporation of about 4 per cent lime in the molten material. A modification of the liming process results in a grade of rosin used in the so-called "gloss oils."

Zinc resinates are also produced by adding zinc to the molten rosin. These products yield varnishes that produce a harder film and are freer from wrinkling and livering than when natural rosin is employed. They also act as dispersing agents and grinding aids.

Rosin Esters.—The most important ester of rosin is ester gum, made by esterifying rosin with glycerine. The accompanying diagram shows the structure that would be obtained by the complete esterification of abietic acid.
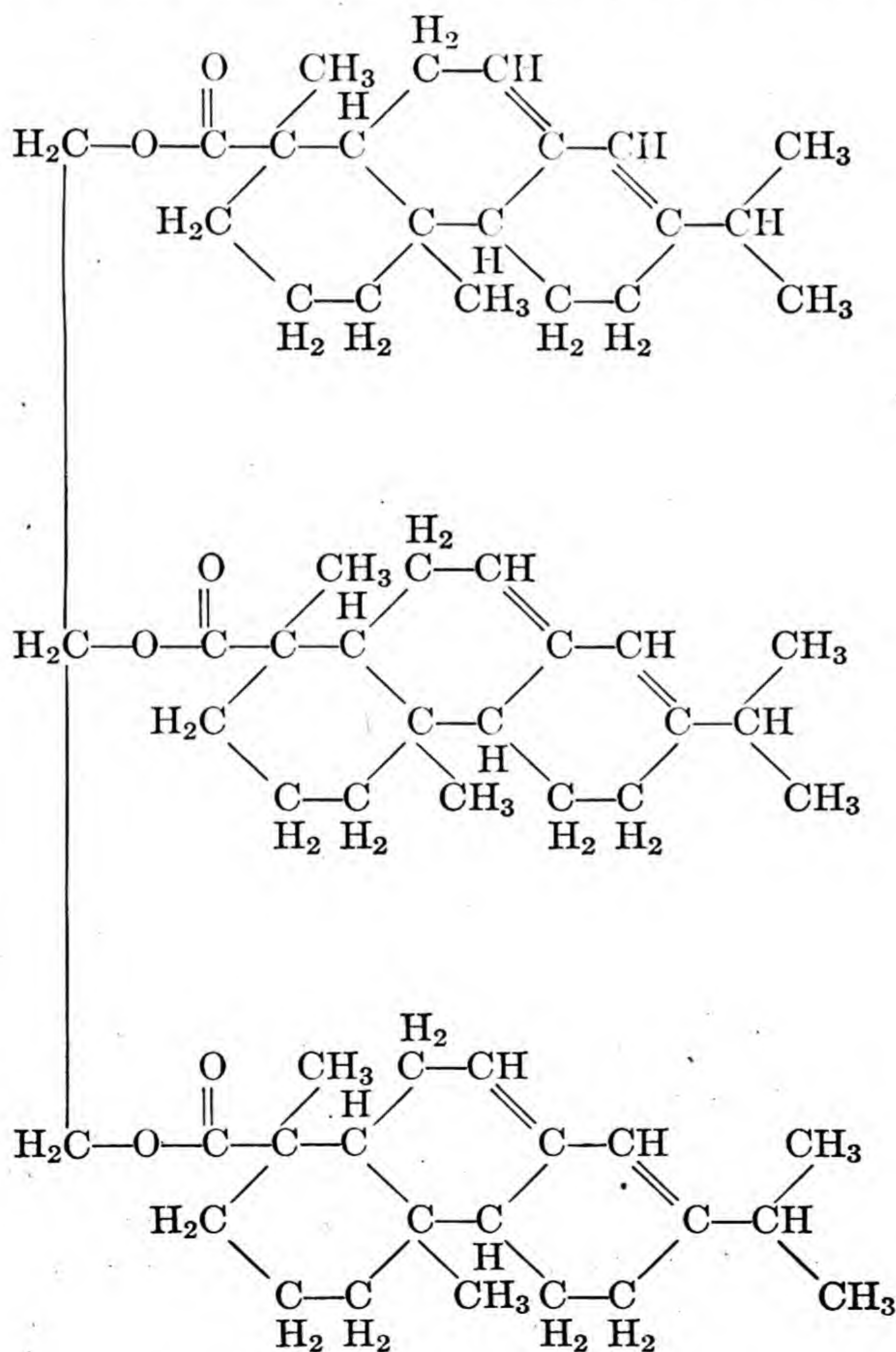
Ester gum has important uses in varnishes, lacquers, special wax additives, inks, etc. It is particularly useful in combination with phenolic and alkyd resins and in the lacquers made from cellulose derivatives.

The manufacturing process is relatively simple. Rosin is heated to about 500°F. and the glycerine introduced in a steady stream over a period of approximately 3 hr. When the glycerine addition is complete, the temperature is raised slightly and a vacuum applied to remove water, glycerol, and decomposition products. The resin is then cooled, broken up, and packaged.

When ester gum was first produced, rosin and the natural resins were the only materials available to the varnish industry. The natural resins were harder to process, and ester gum was definitely superior to rosin in water and alkali resistance so that it soon established an important place among raw materials for the varnish industry. It is still widely used as a relatively cheap resin which can be partly substituted for the more expensive resins and still produce a high-quality product. It has a beneficial effect on the rate of drying and body when combined with other resins.

The methyl ester is produced as a viscous liquid, and methyl dihydroabietate is produced by partial hydrogenation. Both of these compounds are used as extenders in lacquers, in adhesives, and to plasticize mastic compounds.

The ester of diethylene glycol is shown in the accompanying diagram. This resin and the tetrahydro derivative are used as adhesives in combination with starch, dextrin, and casein.
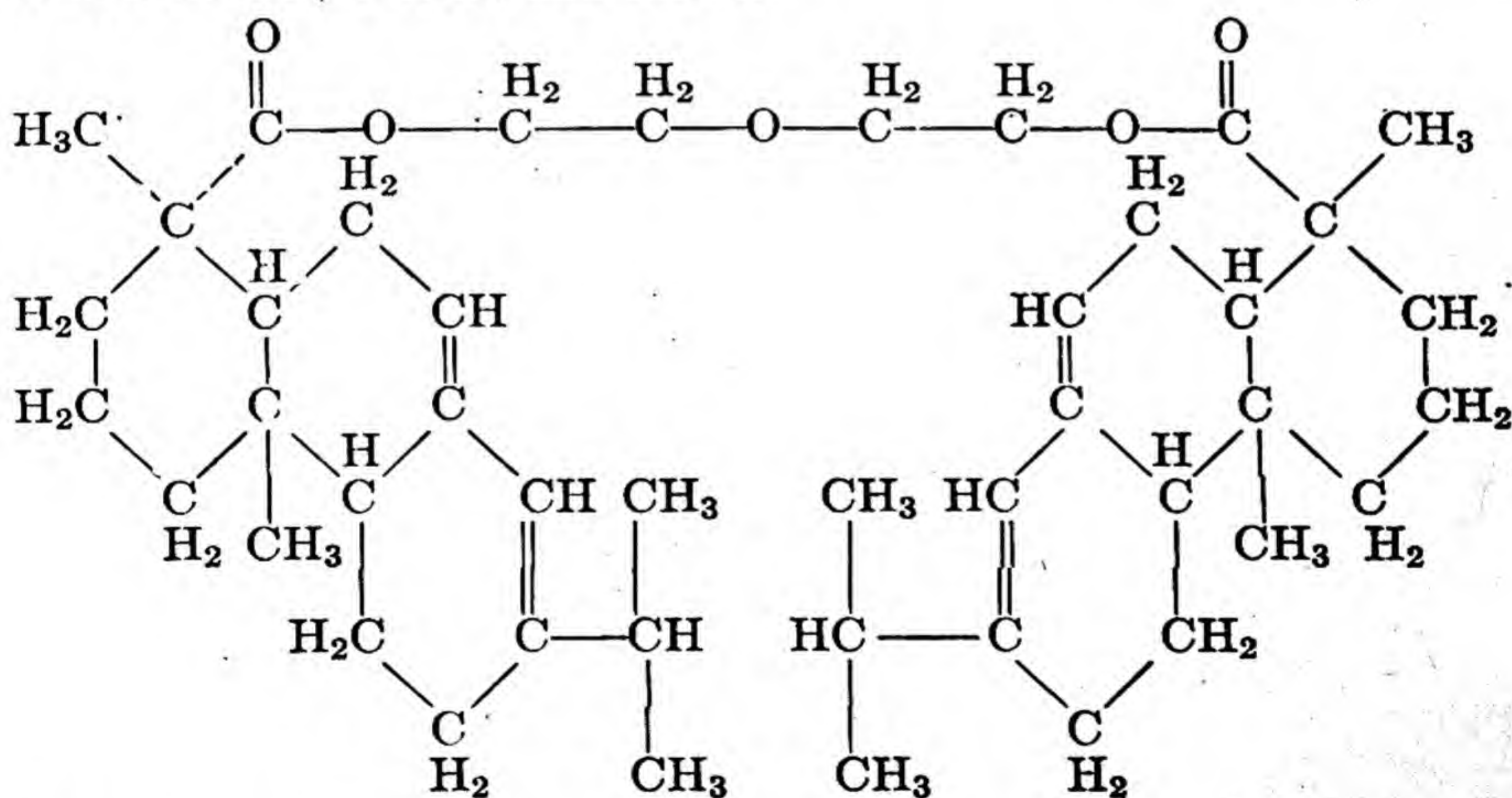
The ester of penta-erythritol has become an important resin within the last few years. The structure of penta-erythritol tetra-abietate is given below. In general, it can be used in place of ester gum with a definite improvement in melting point and heat stability. In combination with

phenol-aldehyde condensates, it forms a series of resins that make excellent durable varnishes.
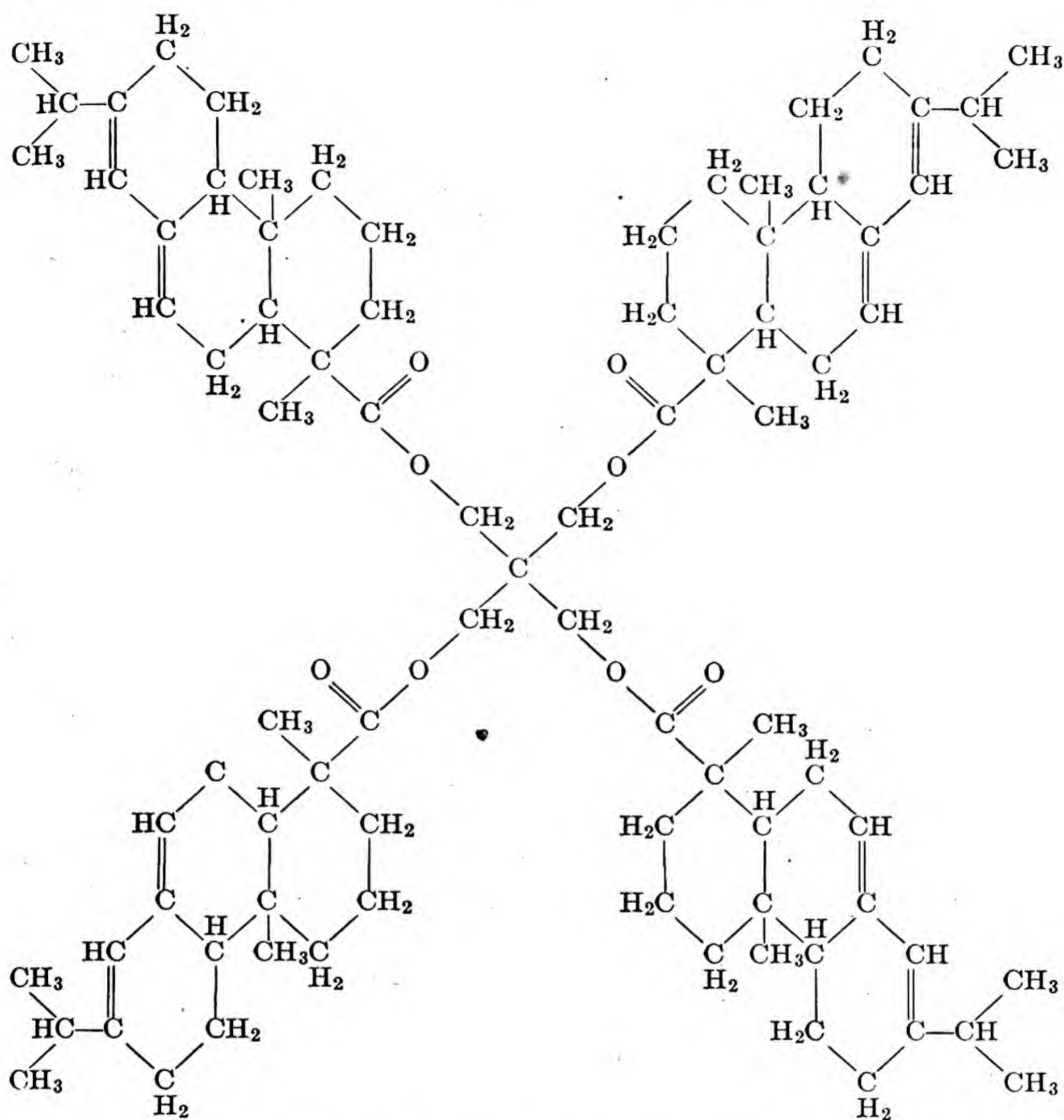
Shellac.—The lac bug, *Tachardia lacca*, produces lac from the soft wood sap trees of India. The insect thrusts its needlelike stinger into the bast wood under the bark and absorbs sap through this tube into the body. At the same time a semipolymerization process is being performed on the sap, and the product is exuded in the form of a gum or stick-lac. During this period the female lays her eggs and the gum is deposited over both the eggs and the bug, finally hardening into a shell which kills the bug. When the young are born some 6 months later, they break through the shell and migrate to other trees to repeat the process. Twice each year a new generation is hatched. The hard crust that is left on the trees is crude shellac.

The lac is not a chemical entity, but is composed of several different

compounds of polyhydroxy acids. None of these compounds is truly resinous when obtained in fairly pure state. The insect produces two types of materials, a hard and soft resin. The harder portion, known commercially as "hard lac," has been separated into various fractions by a series of solvent extractions. About 40 per cent of the hard lac appears to be composed of monobasic interester acids with the formula $C_{32}H_{54}O_9$. Equal proportions of aleuritic acid, $C_{15}H_{28}(OH)_3COOH$, and a mixture of similar acids containing a large proportion of shellolic acid, $C_{13}H_{16}(OH)_2(COOH)_2$, have been isolated from these interesters. The next largest fraction, 20 per cent of the hard lac, contains monobasic interester lactone acids of the composition $C_{15}H_{24}O_5$. The rest of the hard lac is also made up of a mixture of interesters of hydroxy acids. Some of these compounds have molecular weights up to 1,500.

The soft resin can be separated from the hard lac by solvent extraction. This portion has a semiliquid consistency and acts as a natural plasticizer along with the wax. Part of this softer material is composed of a mixture of uncondensed hydroxy acids in which aleuritic and shellolic acids have been found in the greatest proportions. The rest of the soft lac contains lower molecular-weight condensates of aleuritic acid, an isomer of this acid, and shellolic acid. Yellow coloring matter and wax comprise the balance of the crude shellac.

The most common commercial forms of lac are shellac (flakes), button lac (flat disks), garnet lac (dewaxed slabs), bleached shellac, and dewaxed orange shellac. It is also sold as alcoholic varnishes or dissolved in alkaline aqueous solutions.

Shellac has long been recognized as an extremely good rapid-drying finish for woodwork because of the hardness, resiliency, transparency, and brilliancy of its films. These properties have resulted in extensive use as a spirit varnish for floors, bowling alleys, furniture, patterns for metal castings, etc. Bleached shellac gives an excellent clear coating over natural wood, particularly if several thin coats are applied and the surface is carefully rubbed down between coats. Although this process results in a coating of excellent appearance, it is too time consuming for most commercial production methods.

Shellac posses a combination of physical properties that make it an excellent plastic binder for a wide variety of applications. The desirable adhesive or bonding qualities and low dielectric constant have caused it to be used with fillers such as flaked mica or asbestos to produce electrical insulators and forms for coils, etc. The greatest advantage of shellac plastics for electrical insulators is, however, their property of resisting carbonization. The gases generated when an electric arc strikes an insulator made of shellac are poor conductors of electricity and tend to turn the arc away from the composition.

Laminated products are made by coating paper or fabric with molten resin obtained by dusting it upon the fabric as it passes over a hot plate, or by applying alcoholic solutions or aqueous varnishes made by dissolving lac in an alkaline solution.

The resin is compatible with thermosetting materials such as the phenolics and alkyds. Mixtures of shellac and phenolic resins are used in the manufacture of electrical insulators for intermediate voltages. The properties of such mixtures depend upon the relative proportions of the two resins. Those high in lac have good carbonization resistance, while those high in the phenolic resin show a rapid rate of cure and a high resistance of deformation by heat.

The properties of high scratch resistance and resilience make shellac an important resin in the manufacture of phonograph records. Shellac compositions can be worked at temperatures of the ordinary steam table and are readily adapted to the reproduction of records from master dies.

Molding compositions are usually supplied in the form of sheets, which can be softened on a steam table at 225 to 250°F. They are molded at 250 to 275°F. at pressures ranging up to 3,000 lb. per sq. in. Molds must be cooled before ejecting the finished piece. Colloidal dispersions of shellac in water are used as hat binders, paper coatings, leather dressings, machine-belt dressings, photolithography inks, burlap sizes, and many similar applications.

<div align="center">

PROPERTIES AND USES

OF SHELLAC

</div>

Advantages:
    Low dielectric constant
    Good arcing resistance
    Good adhesive properties
    High gloss
    Resilience
    Soluble in inexpensive solvents
    Ability to wet fillers
Disadvantages:
    Low softening point
    Darkens with age
    Poor water and alkali resistance
Common uses:
    Electrical insulators and forms
    Coatings
    Phonograph records
    Adhesives
    Hat binders
    Inks

Lignin.—Lignin comprises about 30 per cent of woody material and is the binder in the growing plant. It is an aromatic organic compound poly-

merized from units containing methoxyl and hydroxyl groups, some of which are phenolic. Waste sulfite liquor resulting from the acid sulfite process of making paper pulp contains dissolved lignin in sulfonated form along with other constituents of wood that are dissolved in the process. Together with other sources in the paper industry, this involves a lignin production of over 2,500,000 tons a year, most of which is burned or run down the sewer. In addition, much larger amounts of lignin are present in sawmill waste and straw.

A large amount of research and development work has been done by government and industrial laboratories on methods of utilizing lignin as a plastic raw material. However, up to the present time no large measure of success has been achieved in using it alone or as a reaction product in a commercial resin. As a plastic, it lacks flow characteristics so necessary for a satisfactory molding material.

Lignin is employed in the field of plastics in two distinct forms, in a lignin-enriched fibrous cellulose as a binder and in powdered lignin resins as extenders. The process for producing the fibrous plastic is based on releasing the lignin bond in the woody material by the action of high-pressure steam without removing or destroying the lignins so that their bonding power may be utilized in the manufacture of board products. The high-temperature steam treatment is essentially an acid hydrolysis, the acids consisting of acetic and formic acids, developed from the woody material itself under the temperatures employed.

The powdered lignin resins are usually made from sulfite waste liquors by acid precipitation. Lignin obtained by this method is used almost entirely in mixtures with phenolic resins. In this capacity it acts as an inexpensive extender without greatly altering the quality or properties of the phenol-formaldehyde resins.

The fibrous material is made by charging wood chips into autoclaves and treating them with live steam at pressures up to 1,200 lb. per sq. in. for a period of a few seconds. In this rapid high-pressure hydrolysis, the autoclaves are usually called "guns" and the chips are considered to be "exploded." The entire cycle, including filling and emptying of the guns, takes about 1 min. In this time the lignins are first softened by the high-temperature steam, and then upon sudden release of the chips to atmospheric pressure, they are exploded by the high internal pressure, resulting in a mass of fibers and fiber bundles, all still containing their natural coating of lignin. The hemicelluloses are hydrolyzed and removed, the cellulose is substantially unchanged, and the lignin has been reactivated so that under suitable conditions it can act as a bonding agent in a manner similar to that which existed in the growing tree.

The fibrous material made by this process is formed into mats and pressed under pressures ranging from 1,500 to 2,500 lb. per sq. in., depending on

the density desired, and at temperatures of 275 to 385°F. Curing times need only be long enough for the heat to penetrate to the center of the sheet. The only plasticizer required is about 4 per cent moisture, which is normally present at ordinary humidities.

The resulting sheet can be surfaced with synthetic resins and colors, or for some industrial applications it can be made without any surface material, considerably reducing the cost of the material for applications where surface resin is undesirable or is not required. It is made in all thicknesses from 0.100 to 2.00 in. and is normally furnished only in flat panels. It has a specific gravity of 1.4 and a compressive strength up to 36,000 lb. per sq. in. Its dielectric properties are good, as is resistance to surface arcing. It may be readily machined and has a lustrous black finish.

Lignin resins are used primarily as extenders for phenolic resins. They have reactive phenolic groups and up to certain maximum amounts, which vary with the type of resin and specific use, can be used as a substitute for part of the phenolic resin in phenolic plastics. As an extender for phenolic impregnating varnishes, the lignin resin can replace up to 50 per cent of the phenolic solids without materially affecting the properties of the molded or cured products. It can be introduced into the initial phenol-formaldehyde reaction, but it is usually put directly into the phenolic resin solution.

CELLULOSE DERIVATIVES

Cellulose is the chief constituent of nearly all forms of plant life and, as such, is one of the most widely distributed and available chemical raw materials. Theoretically, at least, the supply of this raw material is unlimited both as to quantity and location in almost all parts of the civilized world. At present, however, there are only two important sources of cellulose for chemical processing: cotton linters and wood pulp produced by the sulfite process.

Cotton linters are the short fuzz fibers left on the cottonseed after ginning. Cotton is the purest naturally occurring form of cellulose, and the linters are as pure chemically as the staple fiber used by the textile industry. The chemical purification of linters involves a caustic-soda treatment, followed by bleaching. (Cellulose is isolated from wood by various pulp processes, but the sulfite process, in which the noncellulosic constituents are dissolved in an acid calcium–magnesium bisulfite liquor, supplies the bulk of the chemical pulp obtained from wood. A subsequent caustic treatment is necessary to increase the alpha cellulose content to 92 per cent for viscose and 98 to 99 per cent for other types of rayon. A pulping method has been applied in Europe to beechwood, consisting of nitric acid cooking, by which a product is obtained containing 98 to 99 per cent alpha cellulose.
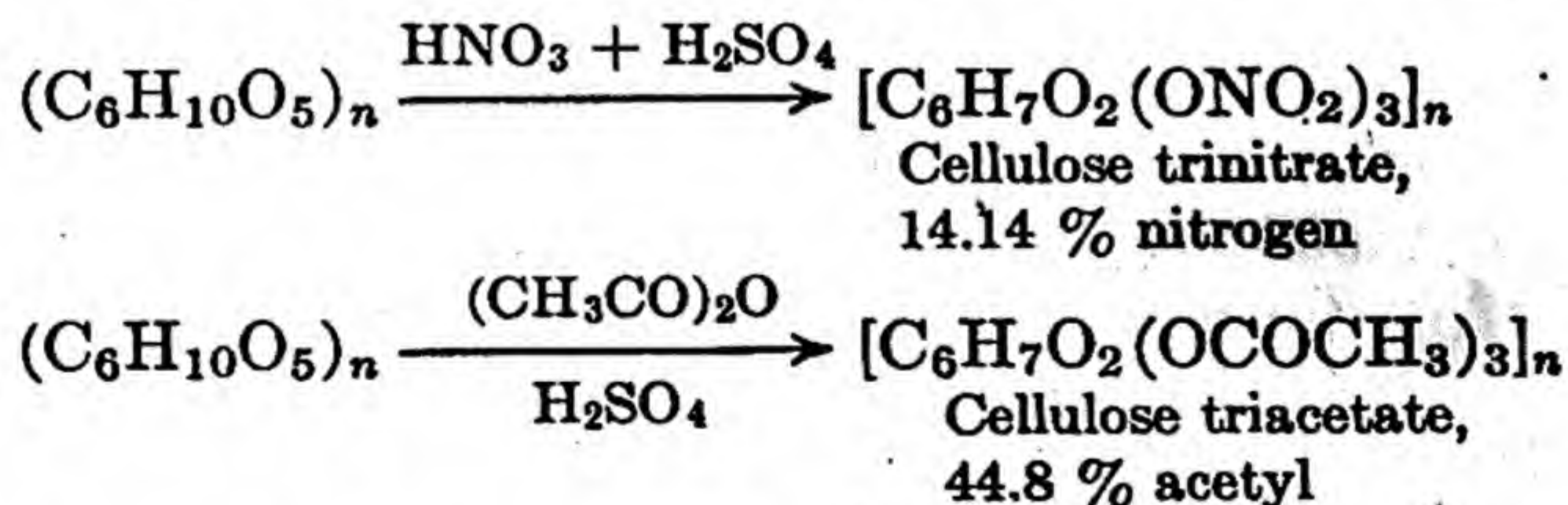
Analysis of highly purified alpha cellulose (C = 44.4%, H = 6.2%, O = 49.4%) leads to the empirical formula $C_6H_{10}O_5$, indicating that cellulose has the compositon of a hexose anhydride. The number of these groups in any molecule determines the degree of polymerization and the molecular weight. Both physical and chemical methods have been used to determine the molecular weight of cellulose. Among the physical methods, the analysis of sedimentation-equ librium data obtained with the ultracentrifuge, measurements of viscosity of cellulose solutions, and osmotic-pressure measurements have yielded important information. The values of the molecular weight obtained by Kraemer using the ultracentrifuge method are sufficient for illustration.[1]

TABLE 5.—MOLECULAR WEIGHT DETERMINATIONS BY ULTRACENTRIFUGE METHOD

Type of cellulose	Molecular weight (weight average)	Number of glucose anhydride units
Native cellulose....................	570,000	3500
Purified cotton linters...............	150,000–500,000	1,000–3,000
Wood pulps........................	90,000–150,000	600–1,000

These values of molecular weights are representative only of the particular samples of cellulose used and may vary considerably, depending on the source and exact treatment of the sample. The molecular weights of the linters and pulp may be much lower than the preceding figures if the samples have been exposed to any but the mildest possible conditions. From these data it is apparent that cellulose is a high polymer and that the molecular weight is affected by methods of isolation and purification.

Nitration and acetylation of cellulose show that each six-carbon unit of the cellulose molecule contains three hydroxyl groups. Both the trinitrate and triacetate can readily be prepared, but higher esters are not known.

$$(C_6H_{10}O_5)_n \xrightarrow{HNO_3 + H_2SO_4} [C_6H_7O_2(ONO_2)_3]_n$$

Cellulose trinitrate,
14.14 % nitrogen

$$(C_6H_{10}O_5)_n \xrightarrow[H_2SO_4]{(CH_3CO)_2O} [C_6H_7O_2(OCOCH_3)_3]_n$$

Cellulose triacetate,
44.8 % acetyl

Complete hydrolysis of cellulose gives an almost quantitative yield of glucose. The relative ease of this hydrolysis is one of the important facts that indicates that cellulose is linked together by glucosidic linkages with one of the ring attachments in the 1-position. Methylation of cellulose

[1] KRAEMER, E. O., *Ind. Eng. Chem.*, **30**, 1200 (1938).

followed by hydrolysis with hydrochloric acid and methanol gives methyl-2, 3, 6-trimethyl-1 glucoside, which in turn on hydrolysis gives a good yield of 2, 3, 6-trimethylglucose. The identification of this product[1] settles the position of the three hydroxyl groups in the glucose unit of the cellulose molecule. These must be in positions 2, 3, and 6. If position 5 is involved in the internal ring, as is the case with glucose itself, the glucose units must be joined in the cellulose chain through the 1- and 4-positions.

Fragments larger than glucose can be obtained by stopping the hydrolysis reaction short of completion. These larger fragments, principally cellobiose, possess the β-glucosidic linkage in contrast to the alpha type of linkage existing in starch. In the following structural representation, the six-membered rings are perpendicular to the paper and the hydrogens and hydroxyl groups are above and below the rings. Thus α-glucose has the hydroxyl group on the number one carbon above the ring. In the beta form it is below the ring.
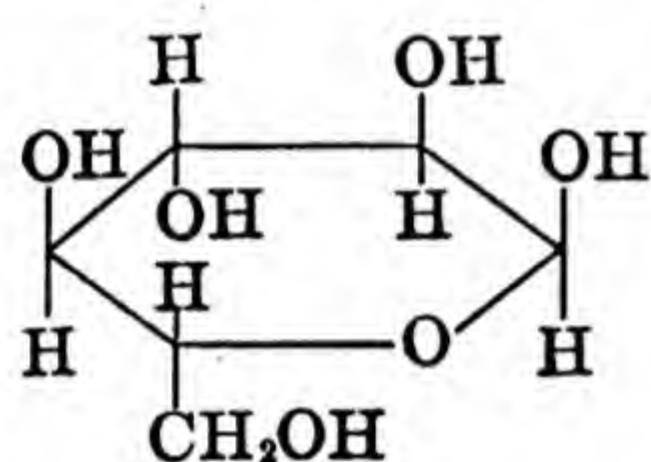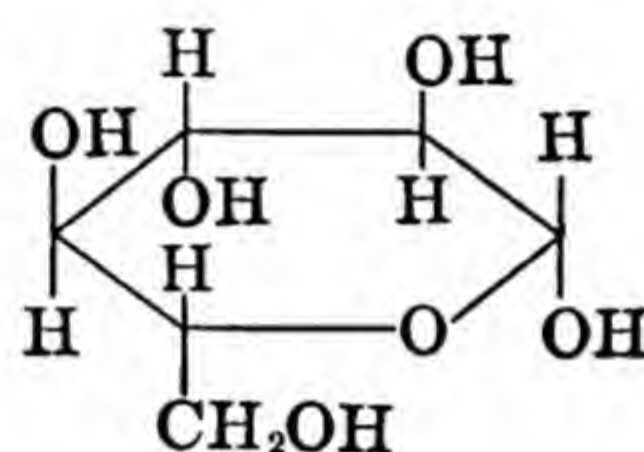
α-Glucose
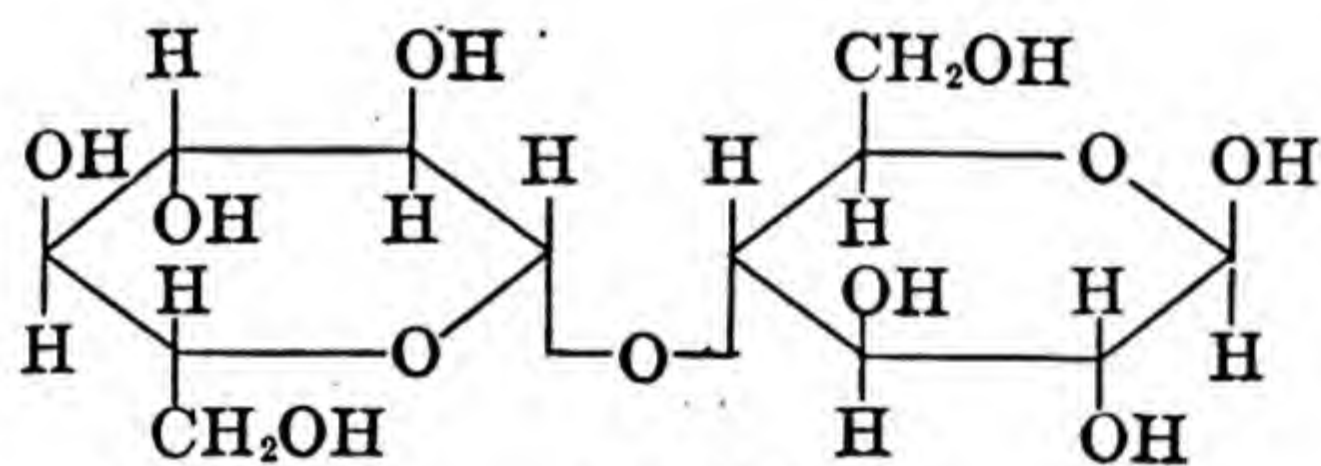
β-Glucose

β-Cellobiose
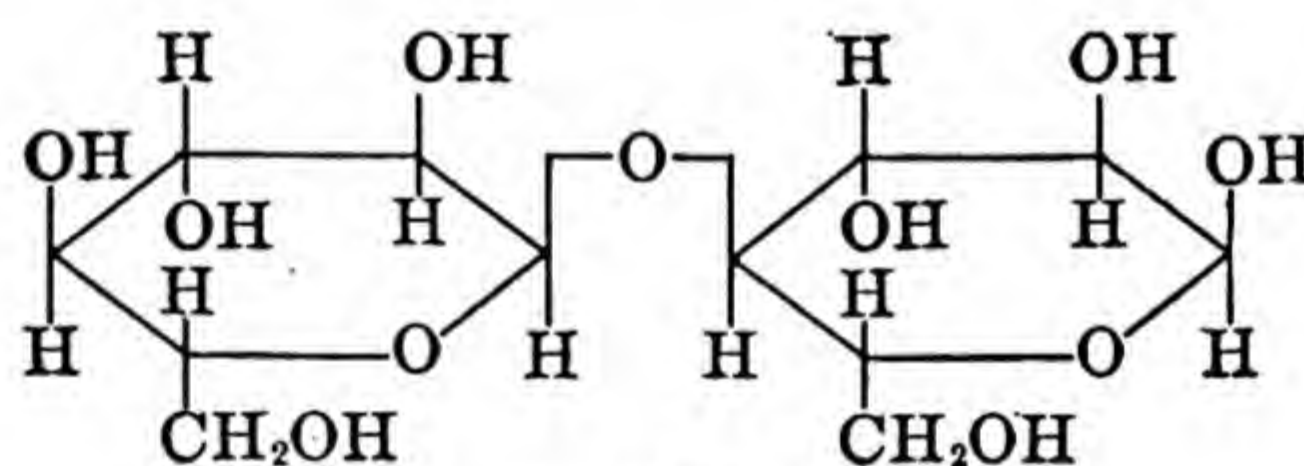
α-Maltose

It is now possible to formulate a configuration of a portion of the interior part of the cellulose molecule chain. It is made up of a number of β-glucose anhydride units linked together by primary valences through oxygen bridges at the 1- and 4-positions, each unit containing three free hydroxyl groups in positions 2, 3, and 6.
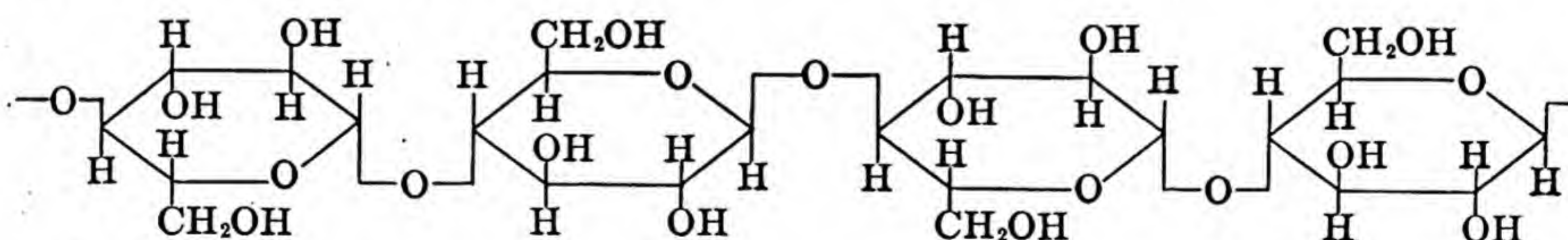
One of these hydroxyl groups is primary, and the other two are secondary. The nature of the groups at the ends of the molecule is also important.

[1] HAWORTH, W. N., and H. MOACHEMER, *J. Chem. Soc.*, 1932, 2372.

It has been possible to isolate from fully methylated cellulose considerable quantities of 2, 3, 6-trimethylglucose and a small but definite quantity of 2, 3, 4, 6-tetramethylglucose.[1] These results alone indicate that at least one of the terminal groups in the molecule must contain four rather than three hydroxyl groups. On the other hand, measurement of the copper number or the iodine number of cellulose obtained by acid hydrolysis of a product of higher molecular weight indicates a certain reducing action by the molecule. In this case, one of the two terminal groups must contain a potential aldehyde group.

Cellulose and its derivatives may be obtained in states of greater or lesser crystallinity, depending on the treatment to which they have been
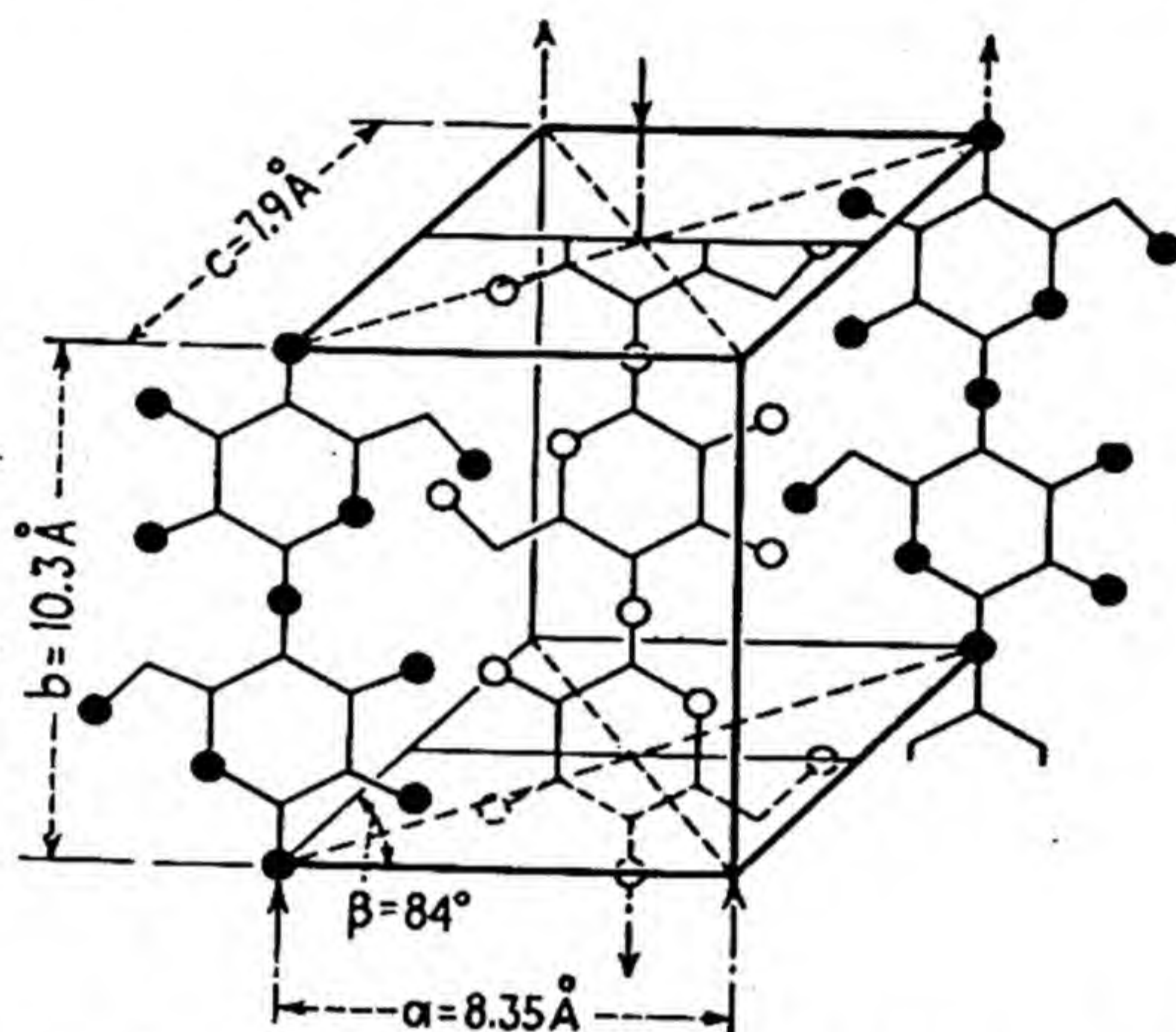
Fig. 44.—Crystal unit of cellulose. [Meyer, K. H., and L. Misch, Ber., 70B, 270 (1937).]

subjected and the extent of substitution. The application of X-ray methods to these preparations,[2] especially those showing a high degree of crystallinity, has been of considerable value in establishing the structure of cellulose itself, the arrangement of cellulose molecules with respect to one another, and the course of cellulose reactions.

The highest degree of crystallinity is normally encountered in native fibers, especially those in which the cellulose chain is deposited parallel to the fiber axis. The structure proposed by Meyer and Misch is shown in Fig. 44.[3] Note that the cellulose chain does not have a center of symmetry and thus may have a different head-to-tail direction. In this crystal-

[1] HAWORTH, W. N., et al., J. Chem. Soc., 1939, 1885.

[2] OTT, E., "The Chemistry of Large Molecules," p. 253, Interscience Publishers, Inc., 1943.

[3] MEYER, K. H., and L. MISCH, Ber., 70B, 270 (1937); Helv. Chim. Acta, 20, 232 (1937).

structure model, the chains run alternately in one direction and then the other.

The crystalline regions in cellulose, although fairly long in the direction of the fiber axis, are not very wide in the perpendicular directions (see Fig. 45). There is no discontinuity between the crystalline regions and the surrounding amorphous material. The long threadlike chains of $C_6H_{10}O_5$ groups may extend from an amorphous region, through the crystallite, and into another amorphous region. In the crystallite, the threads must fall into the definite lattice of the cellulose crystal which is
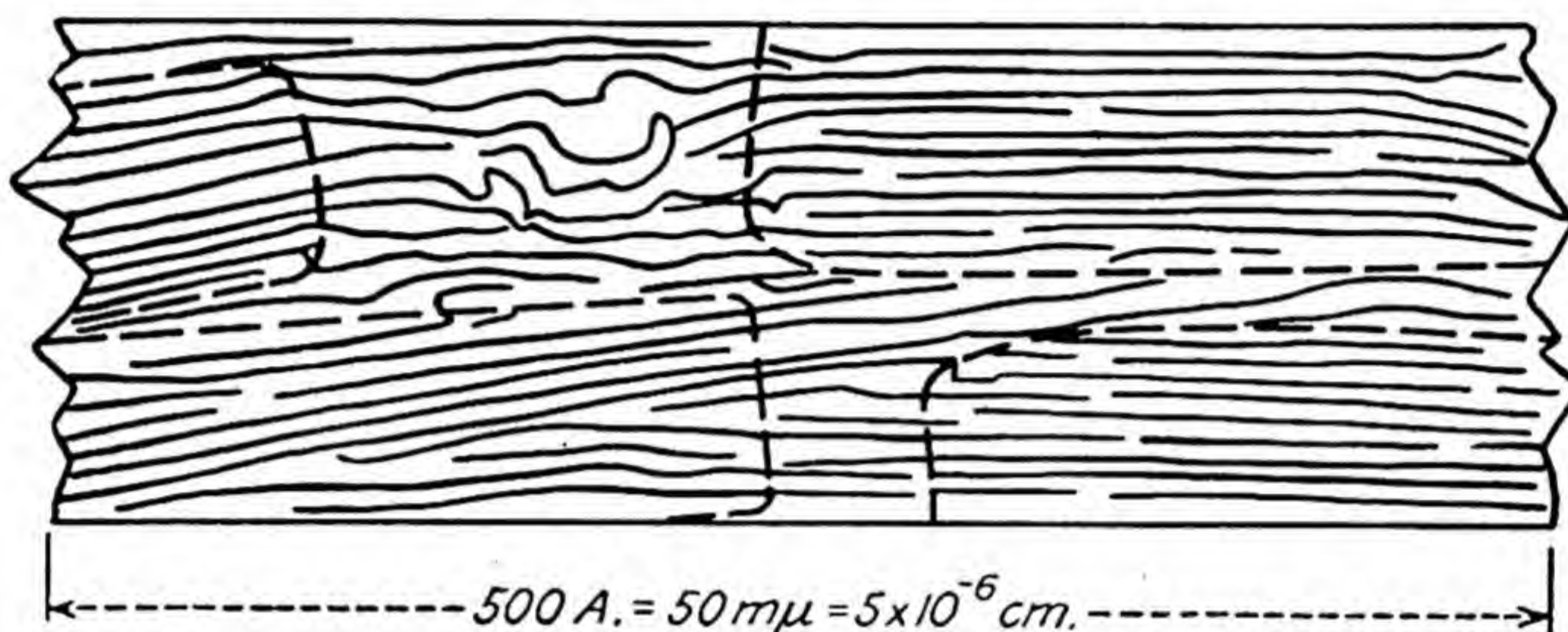
FIG. 45.—Arrangement of linear chains in cellulose. [*Mark, H., J. Phys. Chem.*, **44**, 764 (1940).]

continuously transformed into the surrounding irregular regions. This concept of the cellulose structure has been called the "continuous micelle theory" and is now generally accepted.[1]

In addition to the fine structure of fibers already covered, it should be noted that natural fibers contain channels large enough to carry quite large molecules, such as dyestuffs and acids, throughout the fiber and that there is a system of growth rings visible in the microscope when the fiber is swollen in appropriate reagents. These features of fiber structure are important in determining the course of cellulose reactions as well as the degradation of cellulosic fabrics in service. The relatively large channels serve to bring the reagents quickly to within a short distance of any given point of the fiber. From this point on, the nature of attack is governed by the degree of swelling of the fiber; the greater the swelling, the more rapid the attack. Degradation of fibers by dilute aqueous acids, heat, oxygen, and other reagents giving relatively little swelling leads primarily to attack on the amorphous uncrystallized portions of the fiber, with the result that the fiber falls to powder before the crystallized portions have been severely damaged.

Reactions of Cellulose.—The reactions of cellulose may be divided into two general classes: those involving the hydroxyl groups and those involving the degradation of the cellulose chain.

[1] MARK, H., *J. Phys. Chem.*, **44**, 764 (1940).

REACTIONS OF CELLULOSE

A. Reactions involving hydroxyl groups
    1. Esters
        a. Xanthates
        b. Nitrates
        c. Acetates
        d. Mixed acetate-butyrates
        e. Propionates
    2. Ethers
        a. Alkyl ethers, such as methyl and ethyl cellulose
        b. Hydroxy ethers; methylol ether
   *c.* Ether-esters
    3. Addition compounds with
        a. Alkalies
   *b.* Salts
        c. Acids
B. Degradation reactions
    1. Hydrolysis
    2. Oxidation
    3. Pyrolysis

Viscose.—In the latter part of the nineteenth century, three processes were competing for the newly created synthetic fiber market. Cellulose nitrate rayon was being sponsored by Chardonnet; the cuprammonium process, based on the discovery by Schweitzer in 1857 that cellulose is soluble in cuprammonium solvent, was being developed by the Bemberg interests; and the xanthate process, discovered by Cross and Bevan in 1892, was being exploited by its discoverers. In the early days, the xanthate or viscose process was not so important as the other two; but owing to changes in the economics of the processes, most of the regenerated cellulose rayon, which amounted to 580,000,000 lb. in the United States in 1945, is now produced by this process.

When cellulose is treated with sodium hydroxide solutions of certain concentrations, an addition compound is formed that has some of the characteristics of an alcoholate. One of them is the ability to react with carbon disulfide to form an ester of dithiocarbonic acid (xanthogenic acid) in a manner similar to any other alcoholate.

$$NaOR + CS_2 \longrightarrow C \underset{\diagdown OR}{\overset{\diagup SNa}{=\!\!\!=}} S$$
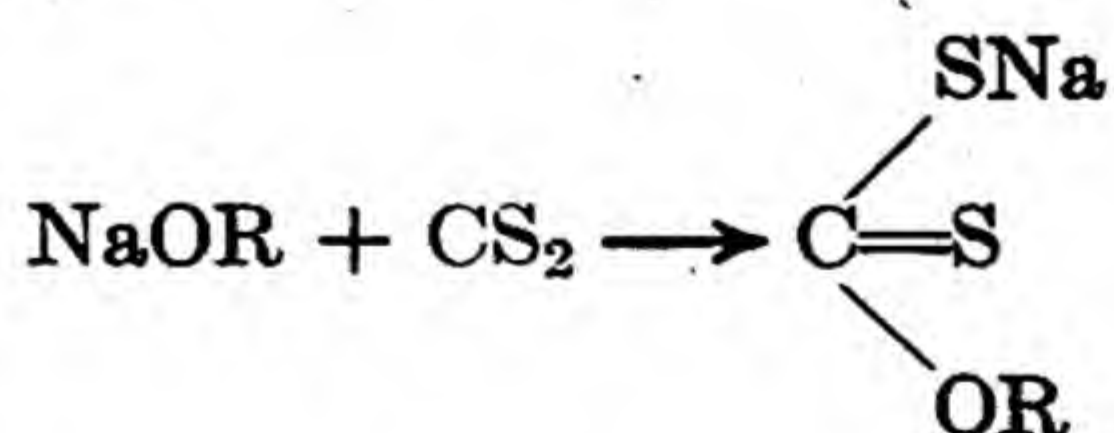
When alkali cellulose is treated with carbon disulfide, a sodium cellulose xanthate is formed.

$$
(C_6H_9O_4)ONa + CS_2 \longrightarrow \underset{O(C_6H_9O_4)}{\overset{SNa}{C=S}}
$$
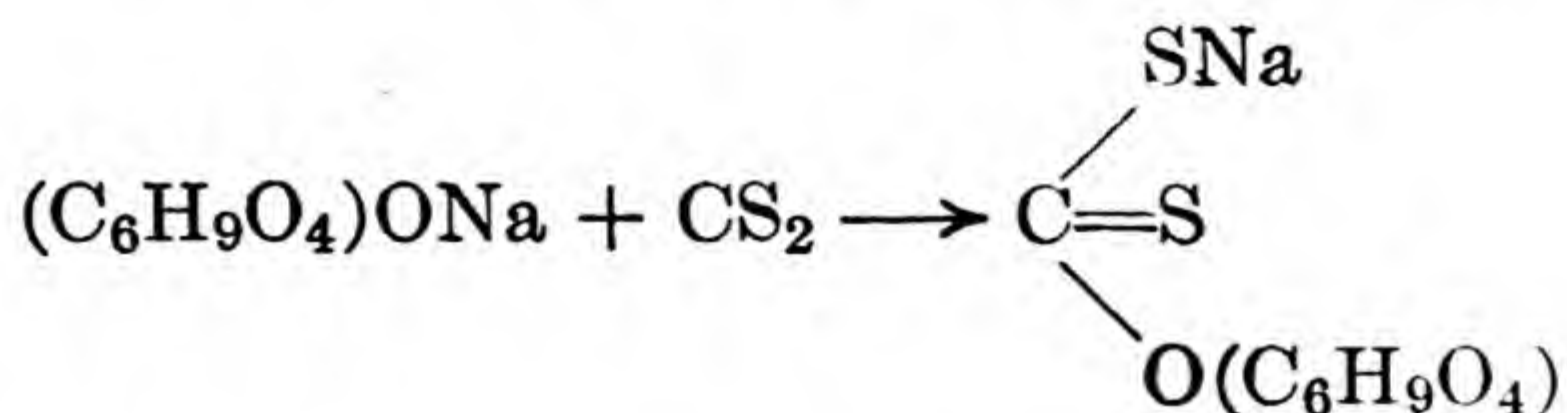
This is an idealized representation of the actual reaction, as only one of the anhydroglucose units is shown and the actual ratio of the $C_6H_{10}O_5$ groups to sodium is nearer two to one. Also there are many possible side reactions.

The xanthate ester dissolves in dilute alkalies to give the so-called "viscose" solution, which is extruded into a sulfuric acid or bisulfate bath for coagulation to regenerated cellulose. The regeneration reactions can be represented as follows:

$$
\underset{OR}{\overset{SNa}{C=S}} + H_2SO_4 \longrightarrow \underset{OR}{\overset{SH}{C=S}} + NaSHO_4
$$

$$
\underset{OR}{\overset{SH}{C=S}} \longrightarrow HOR + CS_2
$$
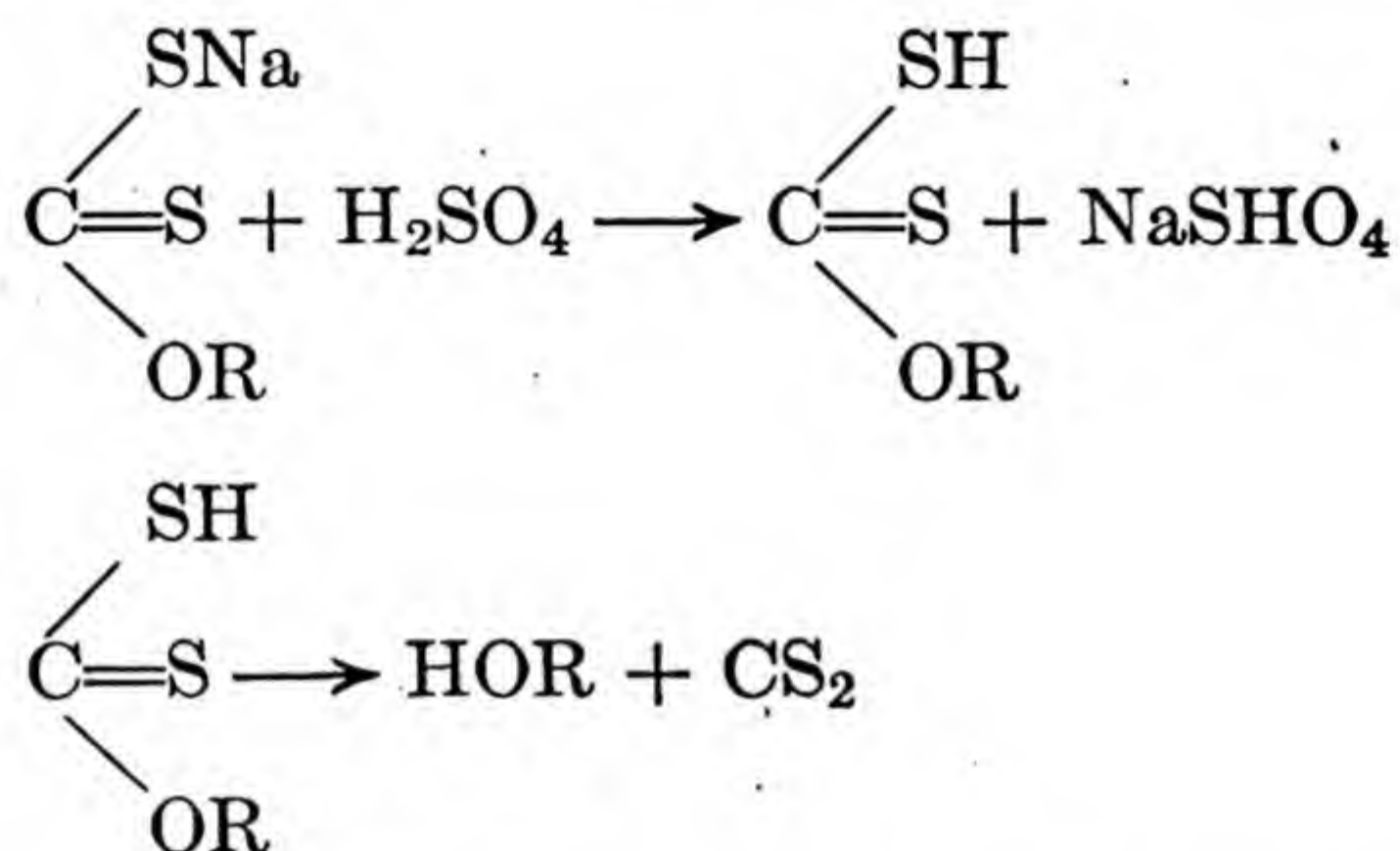
Alkali cellulose is made by treating cotton linters or sulfite pulp with a 17 to 18.5 per cent solution of sodium hydroxide. The pulp is used in the form of sheets, which are placed in a combined impregnating and pressing apparatus. This equipment consists of a rectangular duct equipped with a press ram. The sheets of pulp are placed in the press (see Fig. 46), alkali is added, and about 2 to 4 hr. is allowed for steeping at 15 to 20°C. At the end of this time, the excess alkali is pressed out, and the alkali cellulose is broken up to a loose bread-crumblike material in a shredder or mixer at a constant temperature. The product is then placed in 10-gal. covered boxes and aged at 20 to 25°C. for 48 to 72 hr. All through this process, temperatures are very important and are usually controlled to ±1°C. Temperature has a direct bearing on the viscosity of the finished product. Higher temperatures and longer periods of aging depolymerize the cellulose, giving a finished product of a lower viscosity.

The aged alkali cellulose is then charged into a churn or drum, which is essentially a water-jacketed ball mill minus the balls (see Fig. 47). The cylinder has a capacity of about 300 gal. and will take a charge of approximately 650 lb. of alkali cellulose. The drum rotates slowly, and carbon disulfide is admitted as a vapor under carefully controlled temperature conditions. At the end of the reaction, the orange cellulose
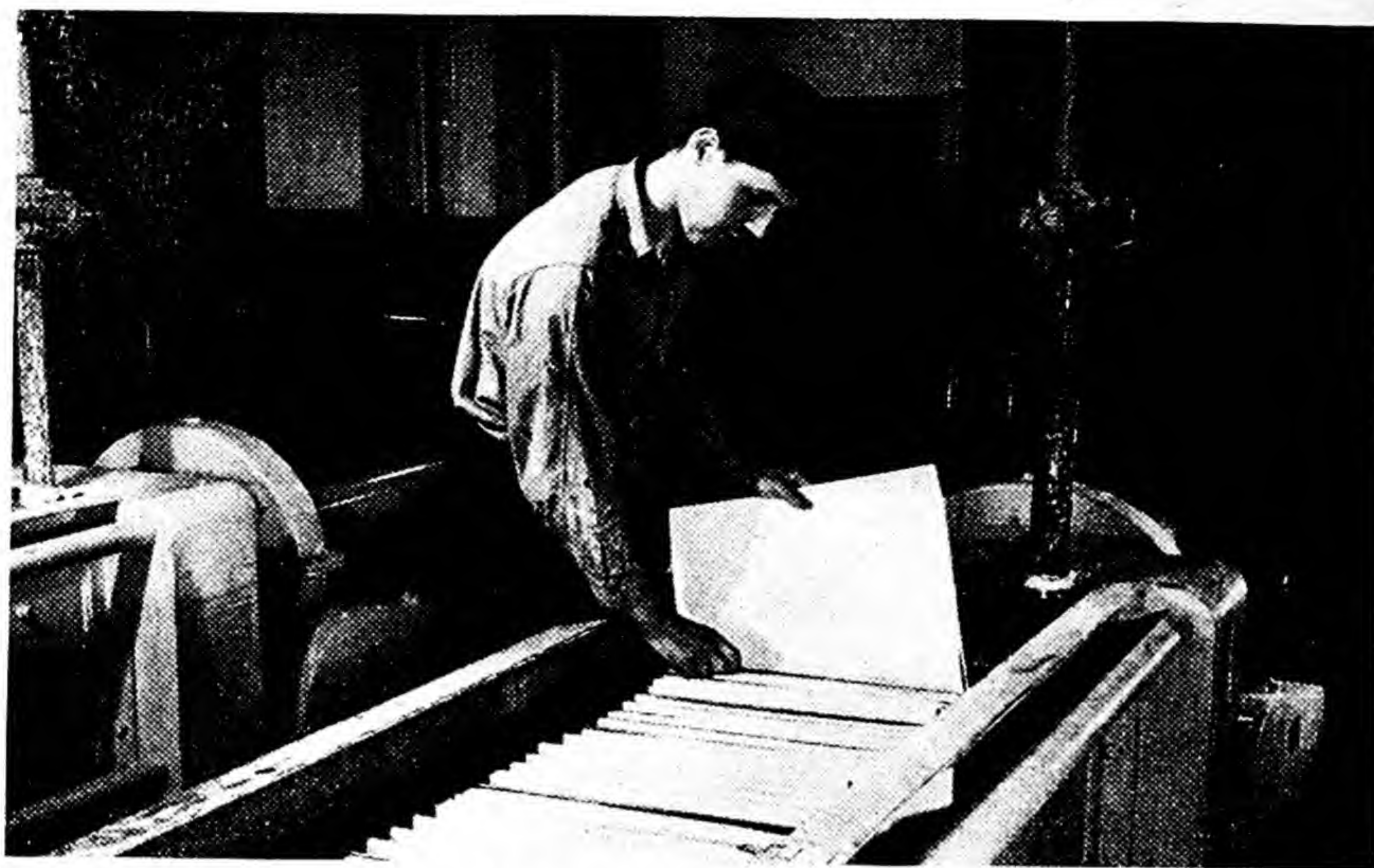
Fig. 46.—Sheets of cellulose being placed in soaking presses for the production of alkali cellulose. (*Industrial Rayon Corp.*)
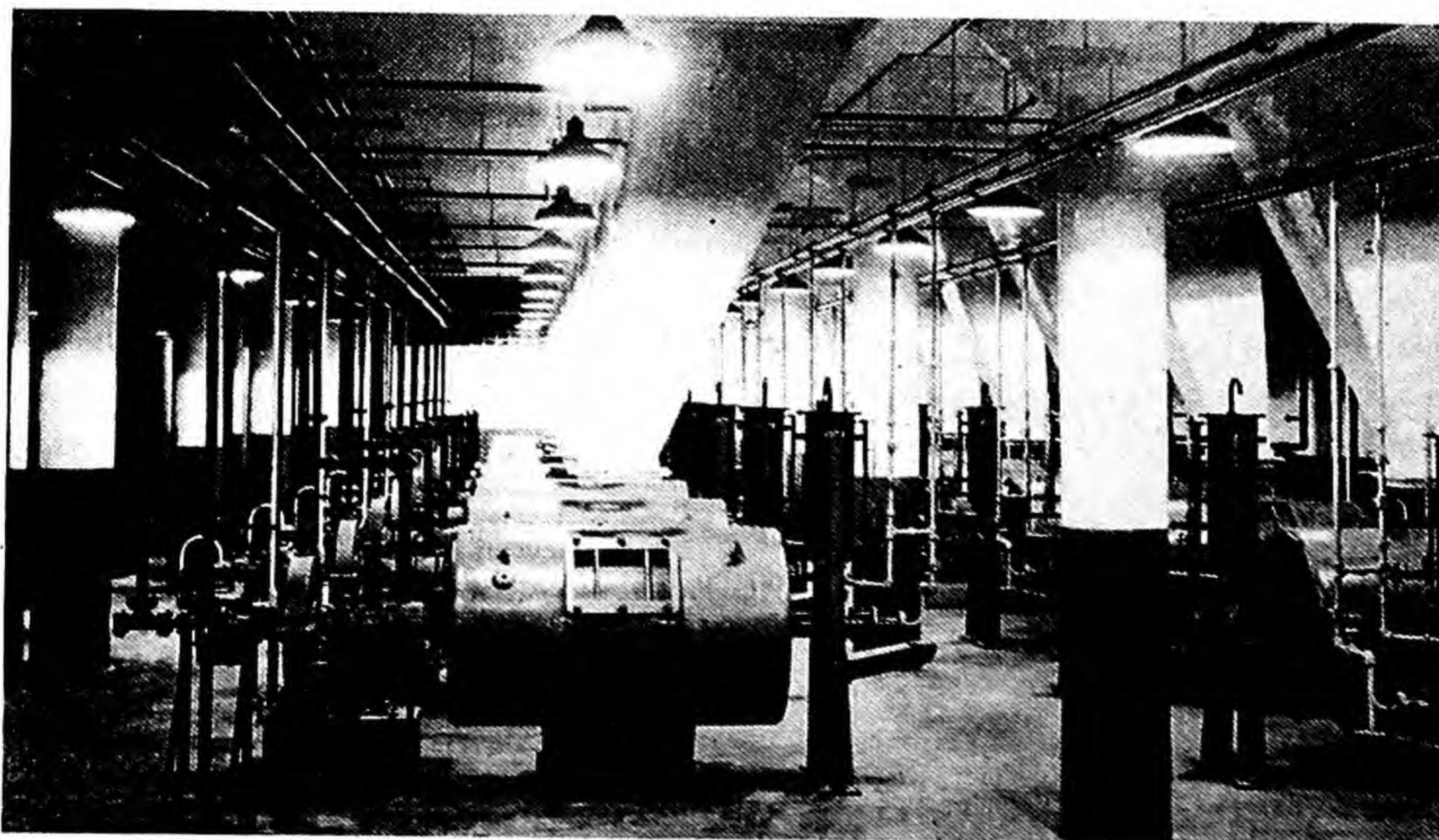

Fig. 47.—Reactors for the production of cellulose xanthate from alkali cellulose. (*Industrial Rayon Corp.*)

xanthate is transferred to a mixer where it is dissolved in dilute caustic to produce a solution containing 7 to 8 per cent cellulose and 6.5 to 7 per cent sodium hydroxide. This mixing is usually done at approximately a con-
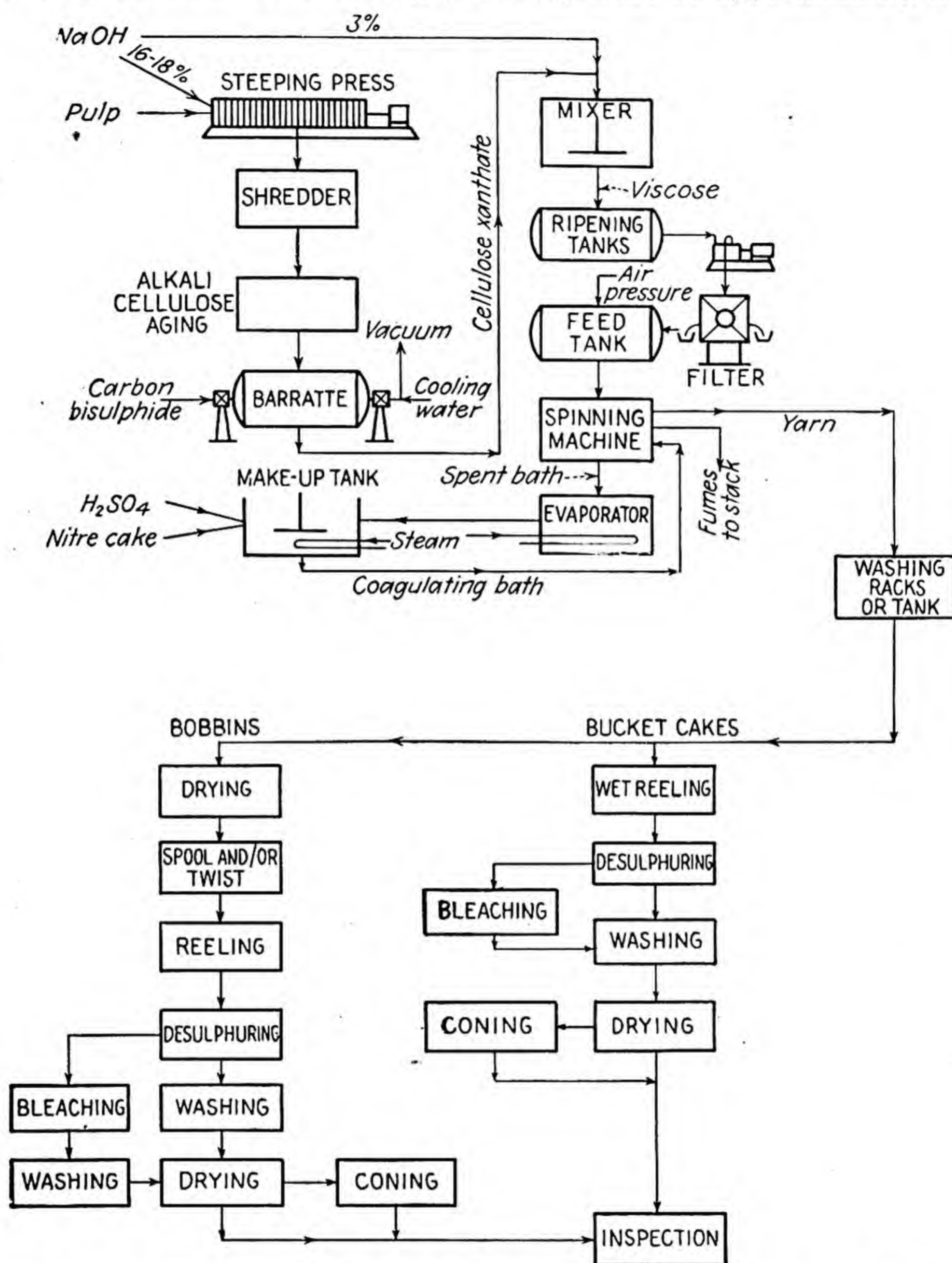

FIG. 48.—Flow sheet for the production of viscose rayon. (*Chem. and Met.*)

stant temperature in the neighborhood of 17° C. The result is an orange-colored viscous liquid, which is the viscose solution. It is ripened for a period of 4 to 5 days, then filtered and deaerated. This solution is fed to the spinning or sheet-forming machines from which it is extruded in the form of filaments or sheets.

In rayon manufacture, the spinning operation consists in forcing the solution through very fine orifices. In the viscose process (see Fig. 48), the spinnerettes are usually made of alloys of platinum and gold and may contain 16 to 60 orifices, depending upon the number of filaments that are desired in the rayon thread. As the solution is forced through the spinnerettes, it comes in contact with a coagulating bath, which consists of sodium acid sulfate. The properties of the coagulating bath are so adjusted that, while each individual jet of liquid is hardened into a filament,
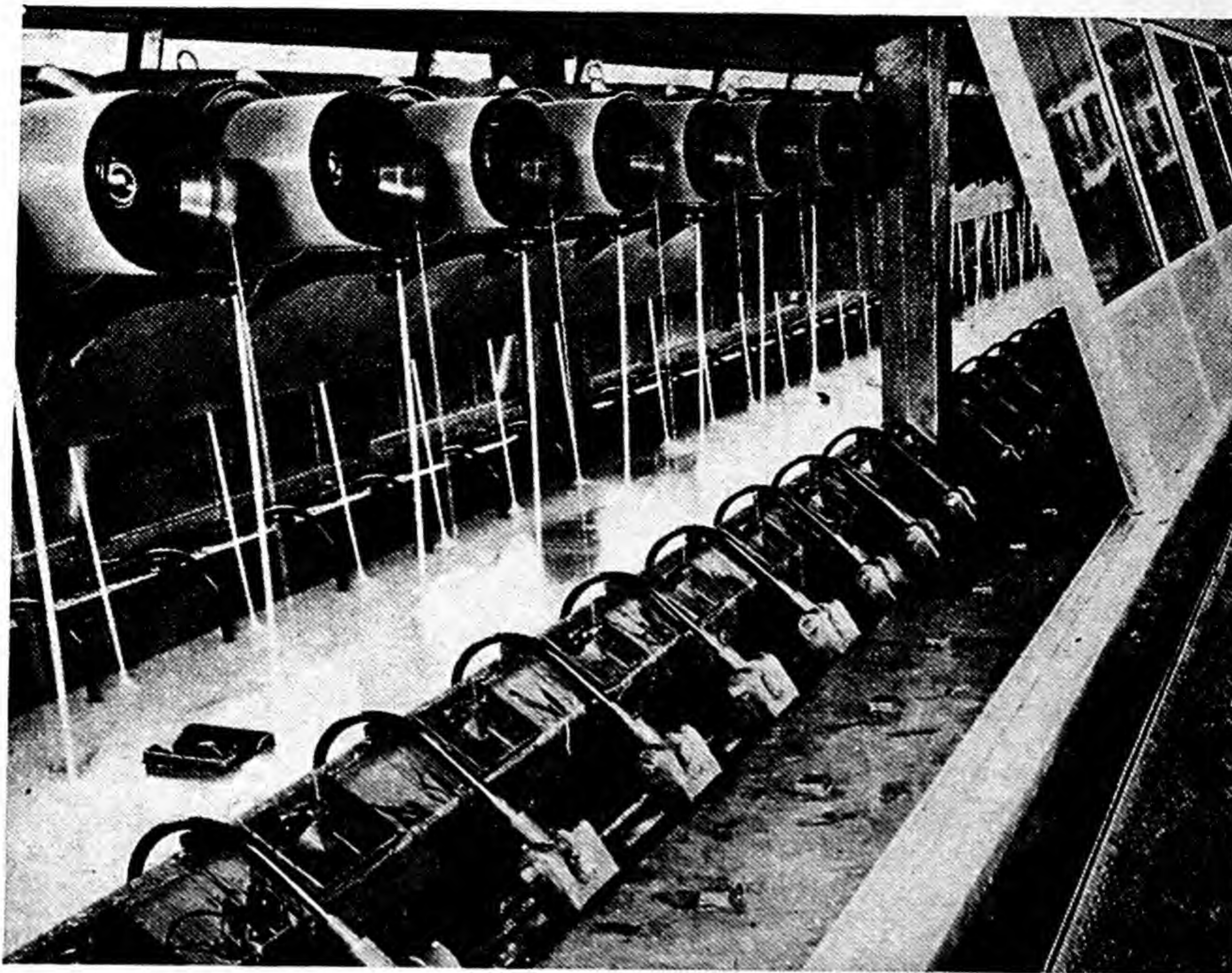
Fig. 49.—Continuous spinning of viscose. Each curved tube carries a spinnerette. The continuous filaments are drawn up to the advancing reels that move the thread forward and pass it downward through openings between the curved tubes to the continuous treating reels shown in Fig. 50. (*Industrial Rayon Corp.*)

these filaments do not stick together but are removed from the bath in any suitable manner and collected either on the outside of a bobbin or on the inside of a perforated centrifugal basket. The fibers are then thoroughly washed to remove the coagulating bath and formed into skeins, following which they are treated with a dilute solution of sodium sulfide to remove any sulfur compounds, bleached, treated with dilute acid, washed, and finally dried. Special surface conditioning agents are also added. Finally the rayon yarn is sorted and inspected.

A new development of oustanding importance is the continuous spinning and processing of viscose yarn (see Fig. 49). In the spool-and-pot

systems, which were the only ones in use up to 1938, the yarn is wound into a package directly from the spin bath. The package is then removed and processed in a series of operations. In the continuous method, the yarn filaments from the spin bath are passed to a series of advancing plastic
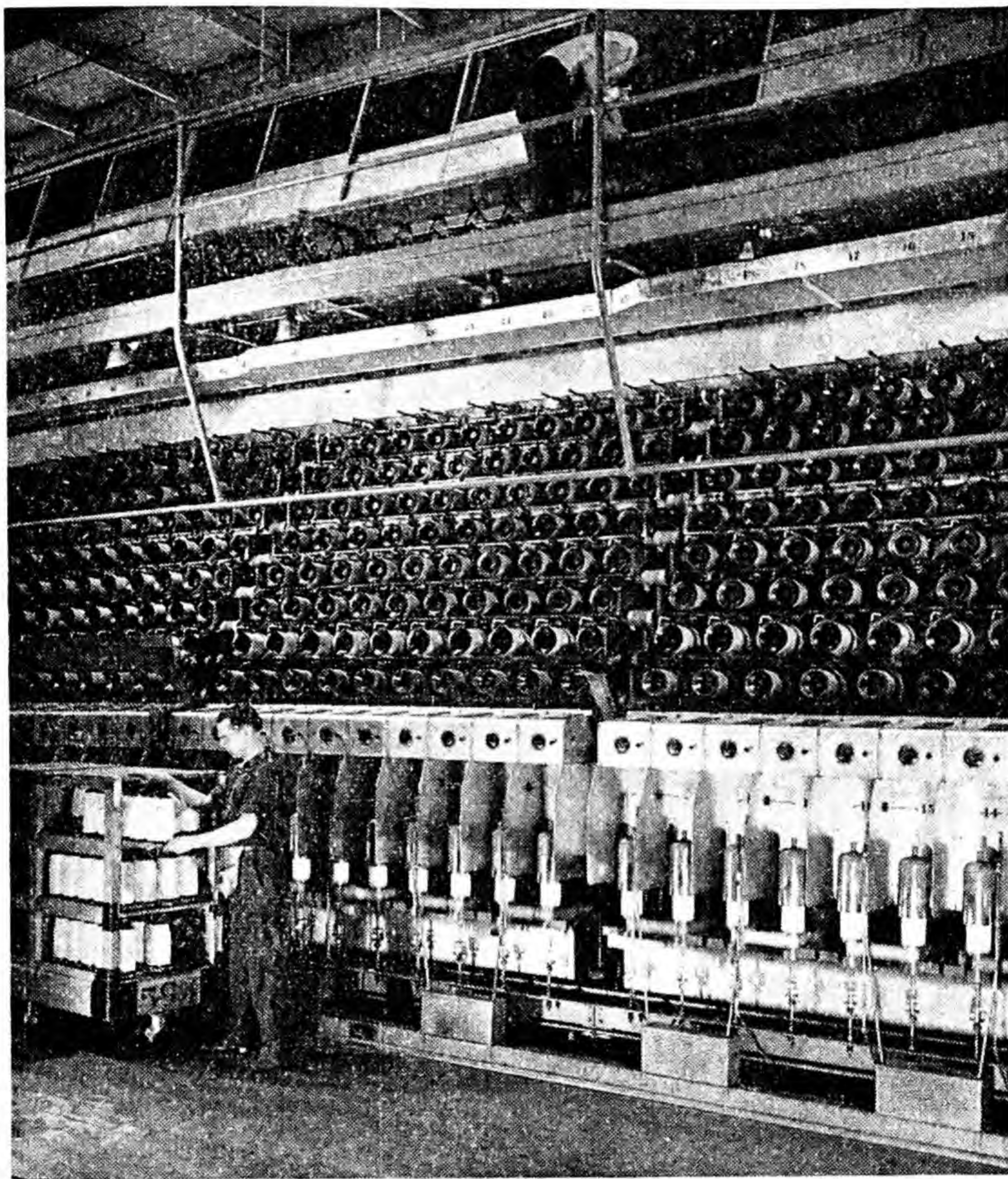

Fig. 50.—A large bank of advancing reels moving the continuous thread of viscose from one treatment to another until it emerges as a bobbin of finished rayon. (*Industrial Rayon Corp.*)

reels (see Fig. 50) for processing treatments of washing, desulfurizing, bleaching, and conditioning. The solutions act on the yarn in a single layer on the advancing reels.

After processing, the yarn is dried by passage over an internally heated aluminum drying reel. Finally, the yarn is given a single twist and wound on 3-lb. bobbins.

The advantage of the continuous process in addition to economy in operation lies in the high quality of the yarn. Greater uniformity and

reduction in knots and broken filaments are claimed. The continuous process has been applied to the production of hi-tenacity yarn for rayon tire cord. The yarn is stretched by changing the gear ratio of the advancing ree's and providing for wider spacing.

Tremendous quantities of viscose rayon and cellophane are produced each year. It is by far the most important rayon and is probably the most versatile of all the rayons, as almost any sheen or appearance may be produced. It takes dyes excellently. Almost any quality may be produced, but the average material is probably somewhat inferior to the acetate rayon, particularly as to wet strength. Both continuous filament yarns and staple fiber similar to cotton are produced for tire cords, particularly suited for heavy-duty tires.

Cellophane is formed on a special sheet-forming machine, invented by J. E. Brandenberger in 1911. This device is made up of a hopper, the bottom of which forms into a nozzle having a long slit as an orifice from which the viscose solution is extruded under pressure into the form of a sheet, which may be deposited on a fabric belt. In a minimum of time and short exposure to air, this film is carried into a solution of ammonium sulfate of carefully controlled concentration and temperature, which coagulates or hardens the deposited film. It then passes through a number of baths consisting of sodium sulfate solution, dilute sulfuric acid, and numerous tanks of water for washing the film.

The regenerated cellulose now appears as a clear transparent sheet. It then passes through a glycerol bath, in which it absorbs approximately 7 per cent of its weight of glycerol, rendering the sheet flexible except at low atmospheric humidity conditions. Other plasticizing agents such as glucose and polyhydroxy alcohols are also used. Most of these plasticizers are chosen because they are hygroscopic and carry moisture into the film. This property is desirable since water is an effective plasticizing agent. The film is then dried by passing it over a series of heated rolls in an atmosphere of hot air.

Since most food packaging requires a wrapping that maintains the initial moisture content of the food, a sheet that prevents the passage of moisture to a very substantial degree is desirable. Before treatment, cellophane permits about half as much moisture to pass through it as a silk handkerchief under identical conditions and is obviously unsuited where low moisture transmission is required. Church and Prindle invented a coating composition in 1927 which, when applied as a very thin layer, is successful in reducing the moisture transmission. The dry cellophane sheet is coated with a solution of low-viscosity cellulose nitrate, plasticizers such as dibutyl phthalate or tricresyl phosphate, resins such as ester gum or dammar, and waxes such as paraffin, ceresin, or certain animal or vegetable waxes, all dissolved in a suitable mixture of volatile organic solvents. After both

sides of the film are coated by dipping, rolls remove the excess and the solvents are removed by drying. The result is the moistureproofed cellophane that is used for wrapping and packaging.

Cuprammonium Rayon.—The cuprammonium process for the production of regenerated cellulose is applied only to the manufacture of rayon fibers. The product, often referred to as "Cupra yarn," can be spun into the finest filament of any synthetic fiber. It has superior wet and dry strength and is particularly suitable for the knitting of very sheer full-fashioned hosiery. Of all rayon processes it is the most complicated, and the production costs are relatively high. However, the product is in demand at premium prices for high-grade fabrics. There is only one producer in this country.

The basic chemical reactions involved in the cuprammonium process are very old. Schweitzer, in 1857, discovered that cellulose could be dissolved in an ammoniacal solution of copper oxide, a reagent that bears his name. Cellulose can be regenerated from the solution by dilution with water or weak acids and bases. Depeisses, in 1890, produced the first commercial regenerated cellulose fibers. Thiele, in 1898, invented the "stretch-spinning process," and later Elsaeser, in applying the method, spun filaments finer than those of natural silk. The first plant was built in Elberfeld, Germany, in 1909.

The accompaning flow sheet (see Fig. 51) indicates the manufacturing and spinning procedure. Copper hydroxide is precipitated with caustic soda or sodium carbonate from recovered liquors to which has been added fresh make-up copper sulfate. It is filtered and charged to vessels provided with scroll agitators. Aqueous ammonia is added, followed by the charge of purified and bleached cellulose. Solution is completed at a temperature not exceeding 24°C. The blue viscous solution is transferred to a tank and diluted with water to give a spinning solution of approximately the following composition:

Cellulose.. 9.0%
Copper.. 3.6%
Ammonia... 7.0%

The solution is filtered and excess ammonia removed by vacuum. It is then pumped to nickel spinnerettes. The filaments are coagulated by passing into funnels through which warm water is flowing concurrently. Considerable stretch is imparted during coagulation. The filaments become hardened, pass from the funnel, and are wound onto bobbins or centrifugal boxes and converted into hanks by a reeling process.

The hanks are decopperized by passing through dilute sulfuric acid, washed with water in a countercurrent system, and dried. The dilute copper sulfate solution obtained from the washers passes to the copper

Fig. 51.—Flow sheet for cuprammonium rayon.

recovery system. In one plant, copper and ammonia recoveries of 90 and 50 per cent, respectively, are obtained.

Considerable development work has been carried out on continuous spinning of cuprammonium rayon. Several years ago the Furness process was operated in this country. In Germany during the Second World War, a continuous process was in the development stage, and a plant in this country has experimental units in operation.

Cellulose Nitrate.—Bracconot first prepared cellulose nitrate in 1833, and Schonbein made a similar discovery independently in 1845, introducing the modern method of preparation. Hyatt prepared collodion in 1861 and obtained patents on celluloid in 1869. Although several workers had at least suggested the use of cellulose nitrate to produce a textile fiber, the credit of being the first to produce a rayon on a commercial scale belongs to Chardonnet, who took out his first patent in 1884. The fiber, made on a relatively large scale by 1891, was not denitrated and burned explosively. For this reason, together with the fact that less expensive processes were developed, Chardonnet silk was rather short-lived.

Although cellulose nitrate did not survive as a textile fiber, it became the first synthetic resin. Celluloid was registered as a trade mark in 1873 and found a ready market for such articles as combs, toothbrush handles, ornaments, and even collars and cuffs. It was, and still is, made by gelatinizing cellulose nitrate with a solution of camphor in alcohol, mixing in the desired fillers, working it between slightly heated rolls, and forming it in presses heated to about 170°F. About the same time, the development of the use of cellulose nitrate in explosives took place.

The completely nitrated product is the trinitrate, with a nitrogen content of 14.16 per cent. The dinitrate would contain 11.13 per cent nitrogen. The various possible products can be classified according to their nitrogen content as follows:

1. *Guncotton.*—13.0 to 13.7 per cent nitrogen, with a degree of polymerization varying from 3,000 to 5,000.

This is military guncotton and is used as a propellant powder. It is the least soluble of all the cellulose nitrates, but will dissolve in acetone and ethyl acetate, yielding very viscous solutions.

2. *Smokeless Powder and Dynamite.*—12.2 to 12.8 per cent nitrogen; degree of polymerization varying from 3,000 to 3,500.

Used for rifle and smokeless powders, and gelatin dynamite. It is more soluble than the higher nitrate but not sufficiently so to use in lacquers.

3. *Soluble Pyroxylin.*—11.5 to 12.2 per cent nitrogen; degree of polymerization varying from 500 to 600. This material is soluble in all common lacquer solvents and can be produced in almost any desired viscosity.

4. *Plastic Grade.*—10.5 to 11.5 per cent nitrogen; degree of polymeriza-

tion approximately 175 to 200. This material is used for plastics and is dispersed by camphor into a plastic gel.

Cotton linters and sulfite pulp are the chief raw materials nitrated to give cellulose nitrate. Other raw materials, or possible raw materials, are cotton waste, rags, and tissue paper.

There are three stages in the preparation of cellulose nitrate: (1) pretreatment of the cotton, (2) nitration, and (3) aftertreatment and dehydration. The cotton is first "teased" or pulled apart by a set of rotating blades and then scoured by boiling in a dilute alkaline solution. The next step is a bleach followed by washing. The cotton is prepared for nitration by removing the water by centrifuging and drying to a water content of approximately 0.6 per cent.

Four factors are of importance in the nitration itself: strength of mixed acids, temperature, time, and the proportion of acid to cellulose. The water content is the most important factor in the preparation of the mixed acid. A very low water content yields a high nitrogen product. Mixed acids vary in composition from 0 to 20 per cent water, 15 to 60 per cent nitric acid, and 30 to 70 per cent sulfuric acid. A large excess of nitric acid is necessary, but the ratio of sulfuric to nitric acid should not be much greater than 3 to 1. Time and temperature are closely related. Within limits, shorter times of nitration can be used at higher temperatures, but the temperature should never exceed about 40°C. as secondary reactions occur, causing instability. Time and temperature also have an influence on the viscosity of the finished product. It is necessary to use about 30 to 50 parts of acid to each part of cellulose, partly because of the bulk of the cotton and partly because of the problem of heat removal.

Two methods of nitration are used:

1. *Thompson displacement method.*—Conical-bottomed stoneware crocks containing a perforated false bottom are used. The cotton is dumped in on the false bottom and the acid added. The cover consists of a perforated plate. After a proper interval, water is run into the top and the acid is drawn off and water added at the same rate so that the acid is displaced by water (see Fig. 52). The nitrated cotton is then centrifuged to remove the excess acid. Because of the displacement of the mixed acid by water, the fire hazard is reduced. This method is used almost exclusively for the production of explosive grades.

2. *Kettle Process.*—The nitrators are covered cast-iron or steel kettles equipped with agitators and cooling jackets. The mixed acid is introduced first and the cotton added to the acid. The reaction takes 18 to 24 min., and the products are dumped from the bottom of the kettle directly into centrifugals and given a rapid whizzing to remove as much of the acid as is feasible. The cellulose nitrate is then "drowned" in a large quantity of water. From the time the material leaves the nitrator until it is drowned,

there is danger of fire, and fires occur rather frequently. Batches are kept small, however, and are segregated as much as possible until they are drowned. The nitrated cotton burns so rapidly that no attempts are made to extinguish such fires.
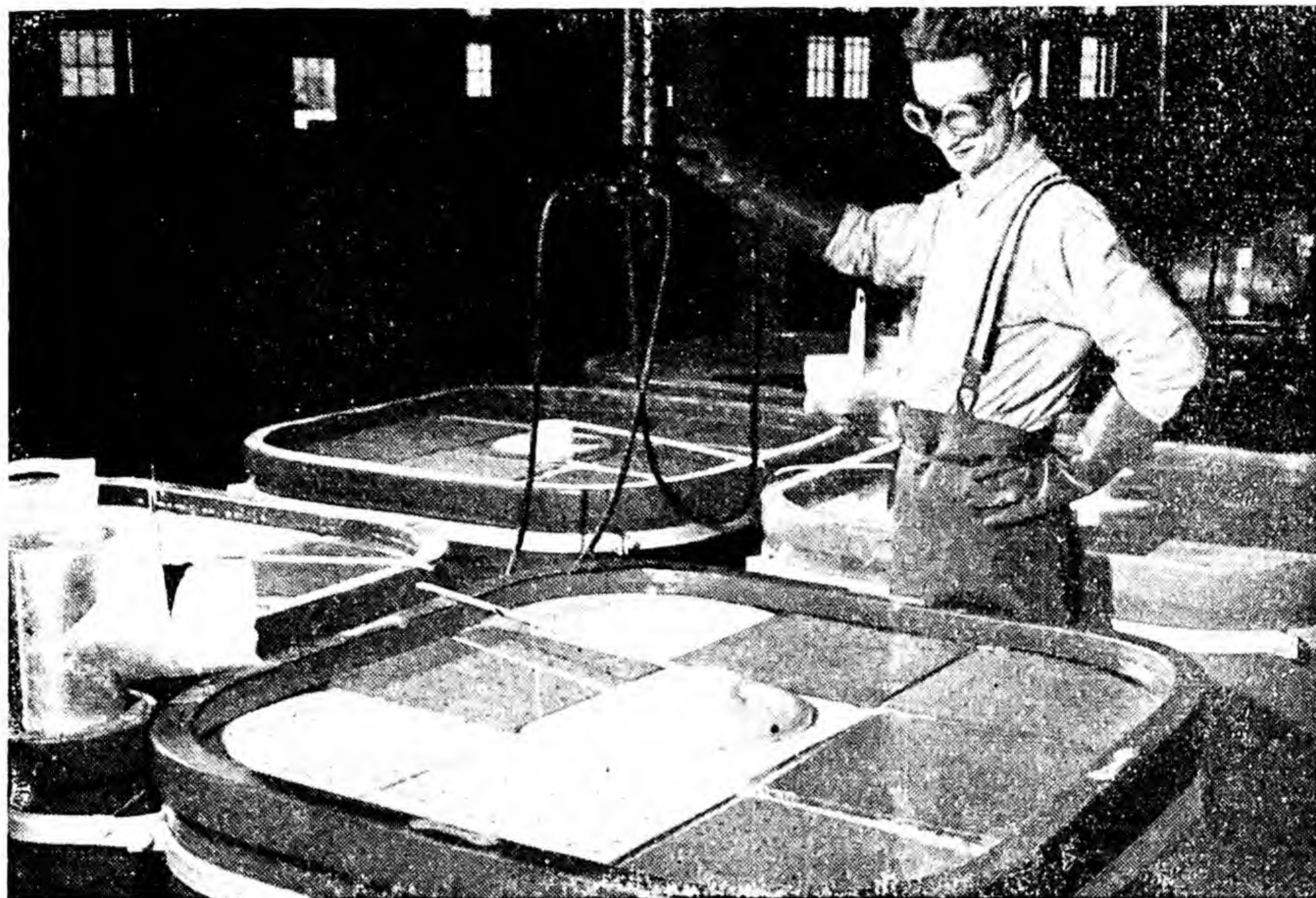

FIG. 52.—Adding water to the top of nitrators in the displacement process for producing cellulose nitrate. (*Courtesy of Chem. and Met. and National Film Board.*)

The drowning operation is common to all nitration methods and may be followed by another whizzing in a centrifugal where fresh wash water is added (see Fig. 53). Then the cotton is "stabilized" by boiling in water for as long as 40 hr. with at least four changes of water. Pulping in an ordinary pulp beater or Jordan machine follows the stabilizing operation, after which additional water is added and the cellulose nitrate is floated over ripples to remove dirt and grit. The next step is the "poaching" operation of boiling in dilute sodium carbonate solution followed by water washes. The extensive washing and neutralizing operations are required to remove all traces of sulfates, which tend to cause instability. Some plants include a measure of control over the viscosity by heating a dilute suspension under moderate pressures. The cotton is then partly dried in centrifugals and completely dehydrated by displacing the water with anhydrous ethyl alcohol (see Fig. 54). Cellulose nitrate containing 30 per cent by weight of ethyl alcohol can be handled safely without much greater danger of fire than that caused by the alcohol.

The finished cellulose nitrate looks very much like cotton but has a
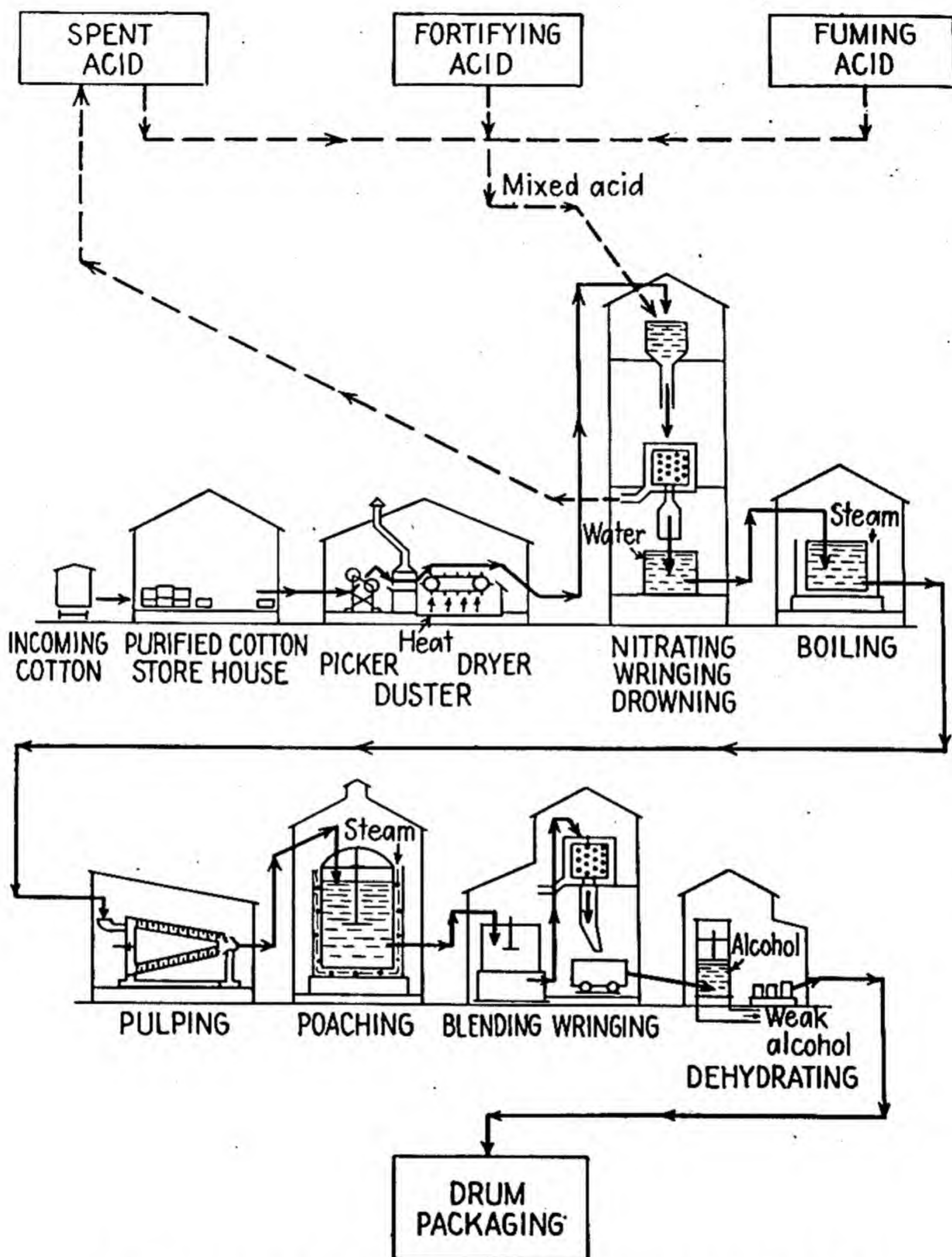
FIG. 53.—Flow sheet for cellulose nitrate. (*Chem. and Met.*)

harsher feel. Large quantities are used in military propellants, for smokeless gunpowder, coatings, and shaped plastic articles. Many of the simpler plastic products are made from cellulose nitrate in the form of celluloid—including products containing plasticizers other than camphor. Cellulose nitrate is one of the cheapest and most shock-resistant thermoplastic resins and finds many uses for that reason.
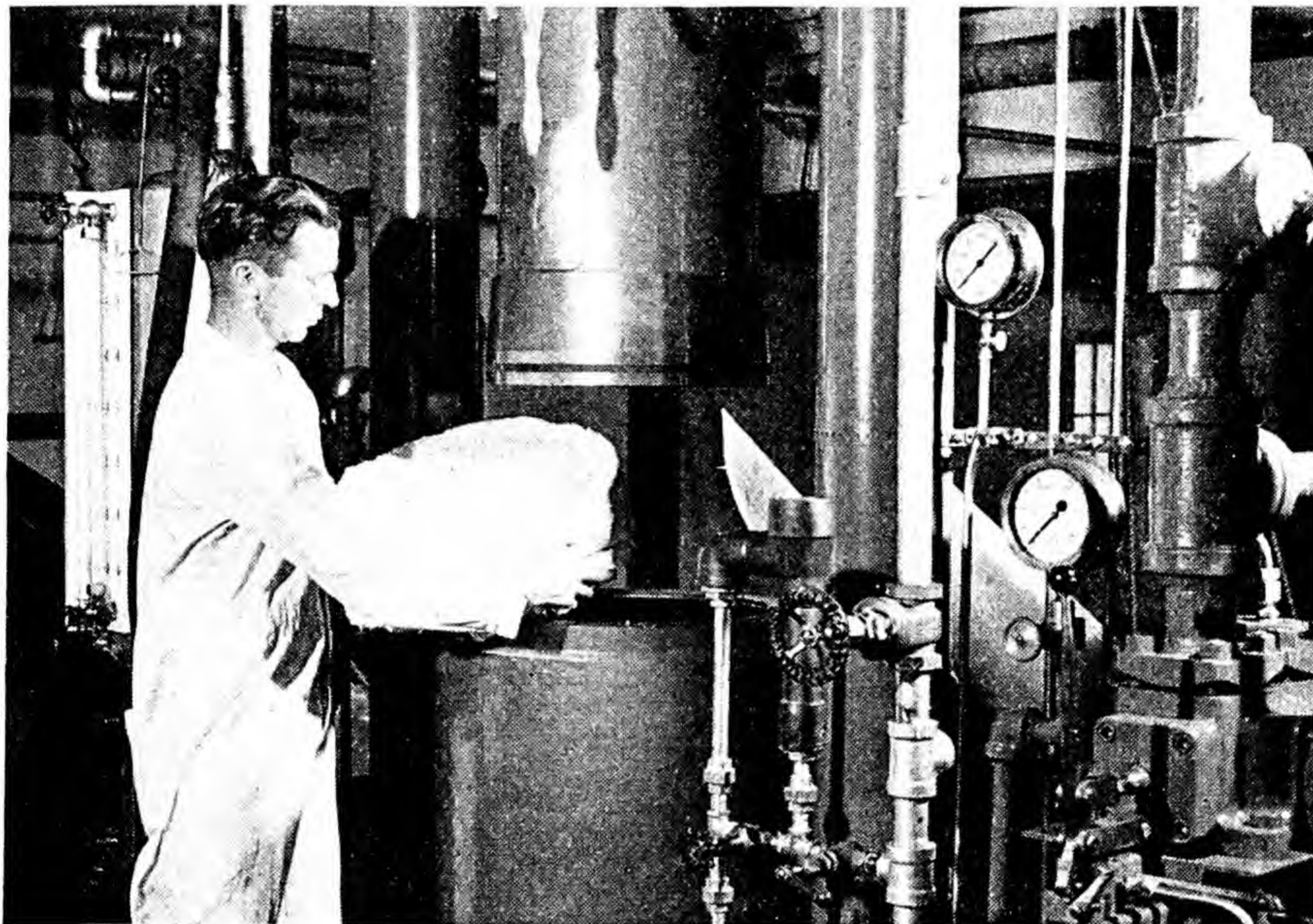
FIG. 54.—Removing cake of cellulose nitrate wet with alcohol from dehydration press. (*Courtesy of Chem. and Met. and National Film Board.*)

Cellulose nitrate is not adapted to compression molding because its easy thermoplasticity makes necessary the chilling of the mold before the removal of the molded article. It cannot be used in injection-molding presses because of its sensitivity to high temperatures. In addition, the added fire hazard, caused by the much greater surface area of granules and powder, has almost completely limited its use to the blocking process or to extruded shapes.

The alcohol-wet cellulose nitrate is first mixed in a dough kneader with camphor and alcohol to a doughy mass, which is worked on heated converting rolls at a temperature of 150°F. Dyes or pigments are mixed in on the rolls to form a homogeneous plastic mass. This material is pressed into solid blocks (see Fig. 55), approximately 6 in. × 2 ft. × 5 ft. in size, or it is extruded. After having been formed into blocks, sheets of any desired thickness from 0.005 to over 1 in. may be sliced off (see Fig. 56).

FIG. 55.—Forming a block of cellulose nitrate plastic. (*Monsanto Chemical Co., Plastics Div.*)

FIG. 56.—Cutting sheets from a block of cellulose nitrate. (*Monsanto Chemical Co., Plastics Div.*)

The sheets and tubes are then seasoned or cured at elevated temperatures to 90°F. to remove the volatile alcohol. The curing period is 2 hr. to 6 months, depending on the thickness of the stock. After seasoning, the material is surface finished.

Cellulose nitrate is manufactured in standard sheets in thicknesses of 0.003 to 1 in. and in sizes up to 20 by 50 in. Rods vary from 52½ to 60 in. in length and ¹⁄₁₆ to 2 in. in diameter. Tubes are 30 to 60 in. in length and ⅛ to 3½ in. in diameter.

Cellulose nitrate plastic products are inexpensive, easily worked, readily machined, swaged, blown, and formed. Practically all colors are available, in transparent, translucent, mottle, and opaque effects. The average specific gravity is about 1.41. It can be fabricated by pressure at 160 to 220°F. and is frequently formed by blowing processes. Cutting, sawing, punching, drilling, drawing, turning, printing, embossing, and polishing may be done with ordinary tools, provided there is a stream of cold water running over the material while it is being worked.

The plastic may be readily cemented to itself by acetone, ethyl acetate, or butyl acetate, and to many other materials by cements containing cellulose nitrate, plasticizers, and solvents. The fact that these simple methods of bonding are available is of advantage in simplifying the fabrication and assembly of many articles.

Cellulose nitrate is practically unaffected by hydrocarbons, animal, vegetable, and mineral oils, and low concentrations of mineral acids at normal temperatures, except that they may gradually remove the plasticizer. It is decomposed by strong alkalies and acids, and dissolved or softened by many alcohols, ketones, and esters. Its resistance to water absorption is not outstanding, but it is superior to the acetate in this respect.

Cellulose nitrate is turned yellow or brown by lengthy exposure to sunlight. It also tends to become brittle, owing to the loss of plasticizers. This difficulty has been overcome to a great extent by using dibutyl phthalate, tricresyl phosphate, or a mixture of other special plasticizers.

Cellulose nitrate in a suitable solvent is used as a household cement. If this type of cement contains aluminum powder, it is known as "liquid solder." The solvents that are used, as well as the nitrate itself, are highly flammable, and long exposure to water causes the adhesive to contract and loosen.

Cellulose nitrate lacquers were developed, in part at least, as an aftermath of the First World War. A good deal of equipment for the nitration of cellulose remained after the large demand for guncotton ceased. In addition, and more important, a relatively large number of chemists were familiar with its manufacture. These facts were the cause of considerable research on methods of manufacture and uses. The most important result was the development of the low-viscosity types. Previously, very dilute

sol.tions were extremely viscous so that it was almost impossible to utilize them as a lacquer. Any quantities that would give an appreciable coat were almost solid gels. With the lower viscosity types, however, it is possible to get enough material into solution to give a very good coat from a solution that is not too viscous to brush or spray. In addition to the development of a satisfactory cellulose nitrate, it was necessary to obtain cheap solvents. During the war the English munitions plants required large amounts of acetone for the manufacture of their propellant powder Cordite. A large share of this acetone was produced in this country by the fermentation process, which also yields large quantities of butanol as a by-product. During the war there was no appreciable market for this alcohol and some of it remained in storage in the early 1920's. This alcohol and butyl acetate were used as solvents for cellulose nitrate lacquers.

The cellulose nitrate lacquers appeared on the market early in the 1920's but were not used to any great extent until they were adopted by the automobile industry in the last half of that decade. They had many advantages over the baking-type enamels previously used. Although more coats were required, the over-all painting operation could be completed in about 12 hr. in comparison to the 48 hr. to 1 week required by the older baking processes. Outside of this advantage, their chief point of superiority was the colors that could be obtained. Since the lacquer base was water white, all the light-colored pigments could be used without masking their brightness by a dark varnish.

Essentially, these lacquers are a combination of four classes of compounds: (1) resins, (2) plasticizers, (3) pigments, and (4) solvents and diluents. Drying consists of evaporation of the solvent only, and no chemical reaction takes place in the film that is deposited. The resins (in the cellulose nitrate lacquers) are cellulose nitrate together with other natural or synthetic resins such as Kauri, ester gum, alkyds, and ureas. Plasticizers are necessary to provide elasticity and avoid brittleness in the film. Tricresyl and triphenyl phosphates, dibutyl phthalate, and camphor are important plasticizers. Many types of pigments are used, both as coloring agents and as fillers. Usually the base solvent consists of esters and anhydrous alcohols. The rate of evaporation or drying of the lacquers must be carefully controlled in order to secure a bright smooth surface. If evaporation takes place too rapidly, the surface will "blush" and the brush marks will set. If it takes place too slowly, the coating will run. To meet all these requirements, a solvent usually contains low- and high-boiling esters, absolute alcohols, and considerable proportions of diluents such as toluene, xylene, or naptha. These diluents are merely used to replace some of the bulk of the solvent with cheaper materials. Although they are nonsolvents for the nitrate, the quantities used are not great enough to cause precipitation.

Cellulose nitrate was the plastic first used between two sheets of glass to produce the so-called "safety" or "shatterproof" glass. It did not stand up under this service, however, as sunlight turned it brown and caused gas bubbles to form until windshields had to be replaced. Other resins have completely replaced it for this purpose.

<div align="center">

PROPERTIES AND USES

CELLULOSE NITRATE PLASTIC

</div>

Advantages:
  Good molding properties
  Availability in all colors
  High impact strength and toughness   .
  Good dimensional stability
  Low cost
Disadvantages:
  Flammability
  Poor electrical insulating properties
  Discoloration and brittleness from exposure to sunlight
  Hardening with age
  Low softening point (140°F.)
Common uses:
  Advertising novelties
  Brush and mirror backs
  Fountain pens
  Piano keys
  Pipe-line wrappings (to prevent soil corrosion)
  Spectacle frames
  Tool and brush handles
  Watch crystals
  Moving-picture film
  Costume jewelry and ornaments

Cellulose Acetate.—The product obtained by the acetylation of cellulose is the triacetate (containing 44.8 per cent acetyl), which may be represented by the empirical formula $C_6H_7O_5(CH_3CO)_3$. Cellulose triacetate itself has not been industrially important, chiefly because of its limited solubility in the common nontoxic solvents. It is, however, produced as an intermediate product in the preparation of commercially useful solvent-soluble acetates. These more soluble secondary acetates are formed by partial hydrolysis of the primary acetate.

Numerous methods for the production of cellulose acetate appear in the patent literature, but only two different types of processes are in commercial use. The distinction between the two lies mainly in the acetylation step.

In the older method, and the one by which the larger part of the cellulose esters is still produced, acetylation is carried out in mixers of the Werner-Pfleiderer type. The mixers are provided with external cooling jackets

and in some cases the agitator blades are cooled to carry off the heat of reaction.

In the second method, which has been developed within the last few years, a low-boiling solvent such as methylene chloride is added to the acetylation mixture and the reaction heat is absorbed by the internal cooling in vaporizing the solvent, which is returned by refluxing to the vessel.

The basic acetylation reaction will be described by referring to the older and more conventional method (see Fig. 57). Cellulose is acetylated with acetic anhydride in the presence of glacial acetic acid and a catalyst, usually sulfuric acid. A large number of other catalysts have been proposed,
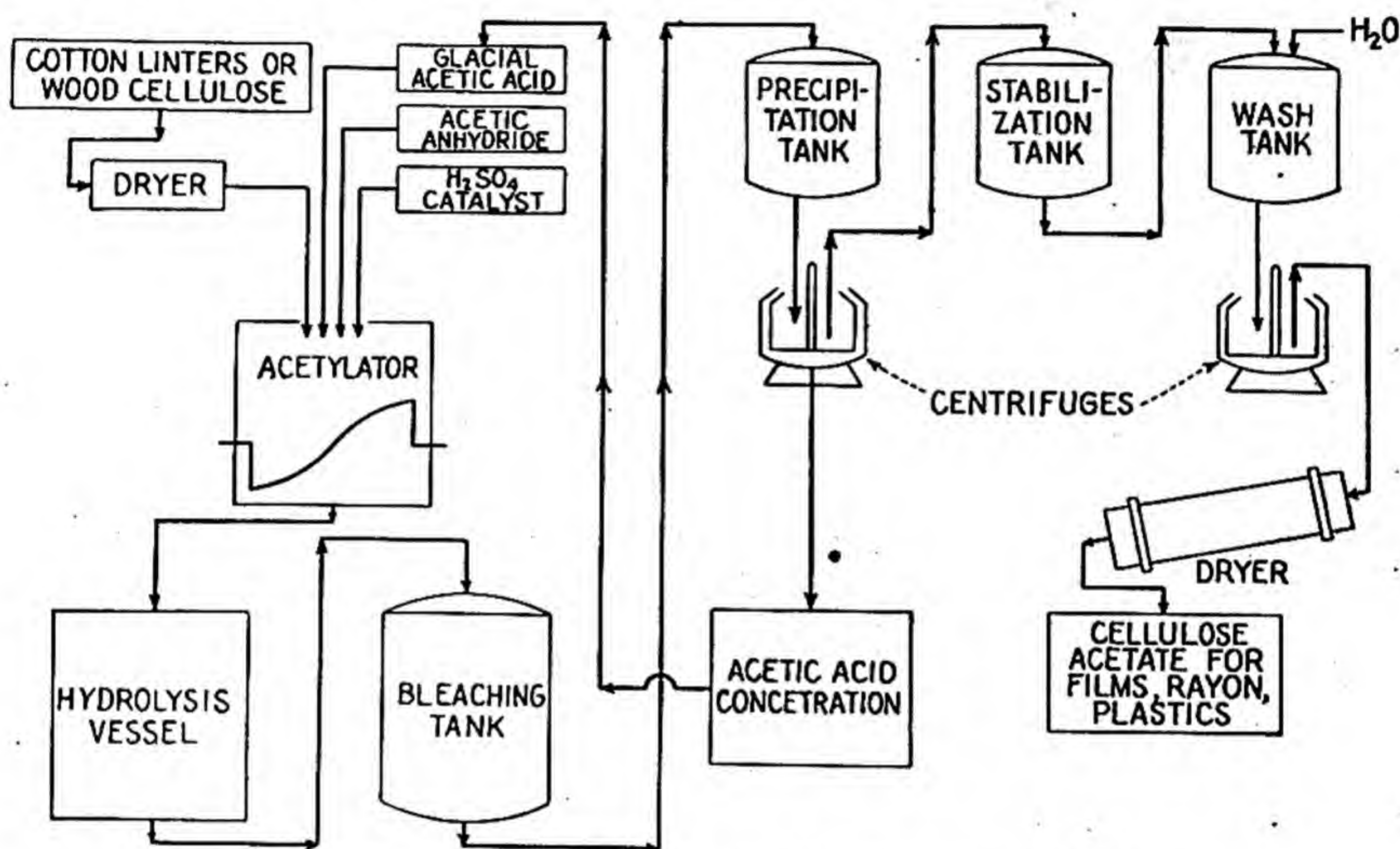
Fig. 57.—Flow sheet for conventional cellulose acetate process.

among them being zinc chloride, perchlorates, mixtures of sulfuric and phosphoric acid, acid sulfates, phosphorus and sulfur chlorides, and sulfonic acids.

While chemically the acetylation of cellulose by acetic anhydride may be represented by a simple equation, the reaction is complicated by the physical and colloidal characteristics of the cellulose and of the cellulose acetate, formed. The esterification reaction proper is accompanied by (1) degradation of the cellulose and (2) dispersion of the resulting cellulose acetate in the glacial acetic acid present. The heterogeneous nature of the reaction mass and the high viscosity of the resulting product require special means of agitation in order to secure uniformity of results. The equipment for this purpose, which must of course be resistant to corrosion by the reagents, sometimes takes the form of a rotating vessel of the ball-mill type, with or without baffles and of varied shapes, and more commonly is a heavily constructed vessel of the dough-mixer type.

The time, temperature of the reaction, and the amount of catalyst used must be carefully controlled in order to obtain the desired product. The cellulose is usually subjected to a pretreatment prior to the acetylation. A large number of pretreatments have been suggested, their principal purpose being to get the cellulose into such a physical form that it will react uniformly. Among the suggested treating agents are formic acid, acetic
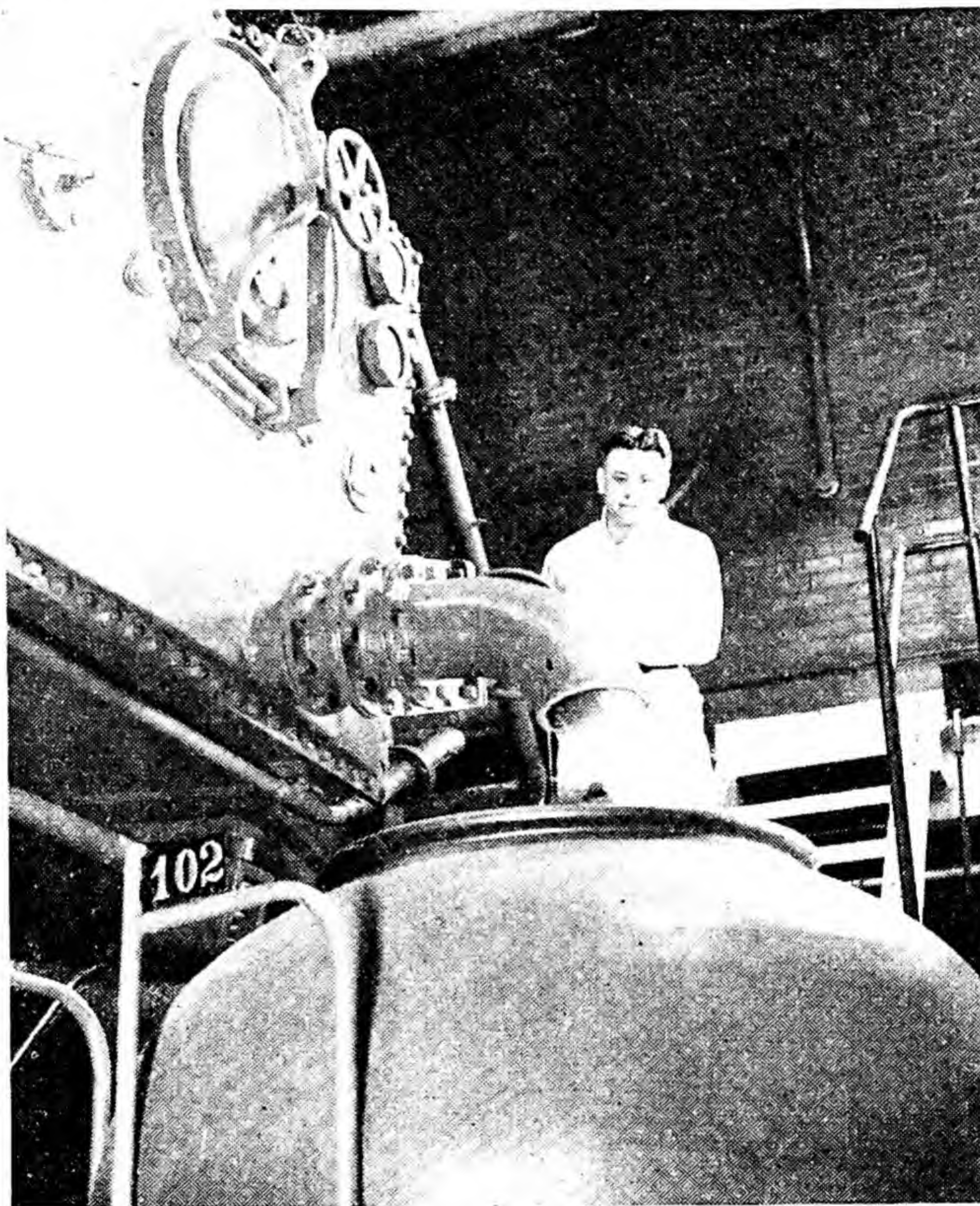
Fig. 58.—Primary cellulose acetate being poured from an acetylator. (*Tennessee Eastman Corp.*)

acid, alkalies, oxidizing agents, sulfuric acid, and lactic acid, but acetic acid with or without sulfuric acid is the only one used in commercial practice.

The primary stage of acetylation is complete when the cellulose is dissolved. When this point is reached, as determined by the disappearance of the cellulose fibers, the resulting clear viscous solution (see Fig. 58) may be diluted with sufficient water or other diluent to precipitate the triacetate, but the triacetate is usually first converted into the secondary

acetone-soluble acetates, which contain between 41 and 37 per cent acetyl groups.

The primary acetate solution is diluted with weak acetic acid. Sufficient water must be present to effect the desired hydrolysis. The amount of water added and the time and temperature of the hydrolysis differ widely in practice. In some cases, this hydrolysis is allowed to take place at room temperature over a period of several days; whereas in others, at an elevated temperature (40 to 60°C.), it may take place in a few hours. The progress of the reaction may be followed by periodically removing samples of the solution, precipitating the cellulose acetate, and determining its composition (percentage acetyl) or observing its solubility in different solvents.

When the reaction has proceeded to a point where a product of the desired composition is obtained, the cellulose acetate is precipitated from the solution. Numerous methods of precipitation have been described. The more common one consists in flowing the viscous acetic acid solution into an excess of water, with suitable agitation, in such proportions that the resulting acetic acid is below the concentration that will soften the cellulose acetate. The dilute acid is sent to the recovery process, and the precipitated acetate is washed with water until it is acid free, after which it is dried under controlled conditions.

In some cases, the precipitated material is subjected to bleaching and stabilization treatments, the purpose of the latter being to destroy or remove the residual sulfuric acid catalyst, which if allowed to remain, even in traces, tends to produce color in the final product.

The cellulose acetate thus prepared is a white fibrous or flaky material. The cellulose acetates of commerce are characterized by two important properties: (1) viscosity, usually measured in acetone solution; (2) composition, as percentage of acetyl. The range of possible viscosities is rather wide, permitting the adaptation of the product to various uses. The usual range of acetyl values is between 37 and 41 per cent, solubility in different solvents being dependent upon the precise composition.

In addition to the foregoing variable properties representing the type of the cellulose acetate are certain others that indicate its stability, uniformity, and general quality. An acetate is usually examined with respect to its moisture content (which may be as high as 6 per cent, depending upon relative humidity conditions), the free acid present, the stability toward heat or toward hydrolysis, the completeness of its solubility in the solvent (usually acetone) in which it is to be used, and the color or clarity of the resulting solution.

In applying the acetylation method using methylene chloride as the internal cooling agent, large batches can be made since the size of the

vessel is not limited by the physical requirements for external cooling. A typical batch is as follows:

		Pounds
Cellulose		7,700
Acetic anhydride		23,100
Acetic acid		5,400
Methylene chloride		10,000
Sulfuric acid		77

Acetylation requires 4 to 6 hr. at 50°C. The flow sheet (Fig. 59) shows the subsequent steps, including distillation and recovery of the methylene chloride, hydrolysis, precipitation, cutting, draining, continuous washing, centrifuging, vacuum drying, and blending.
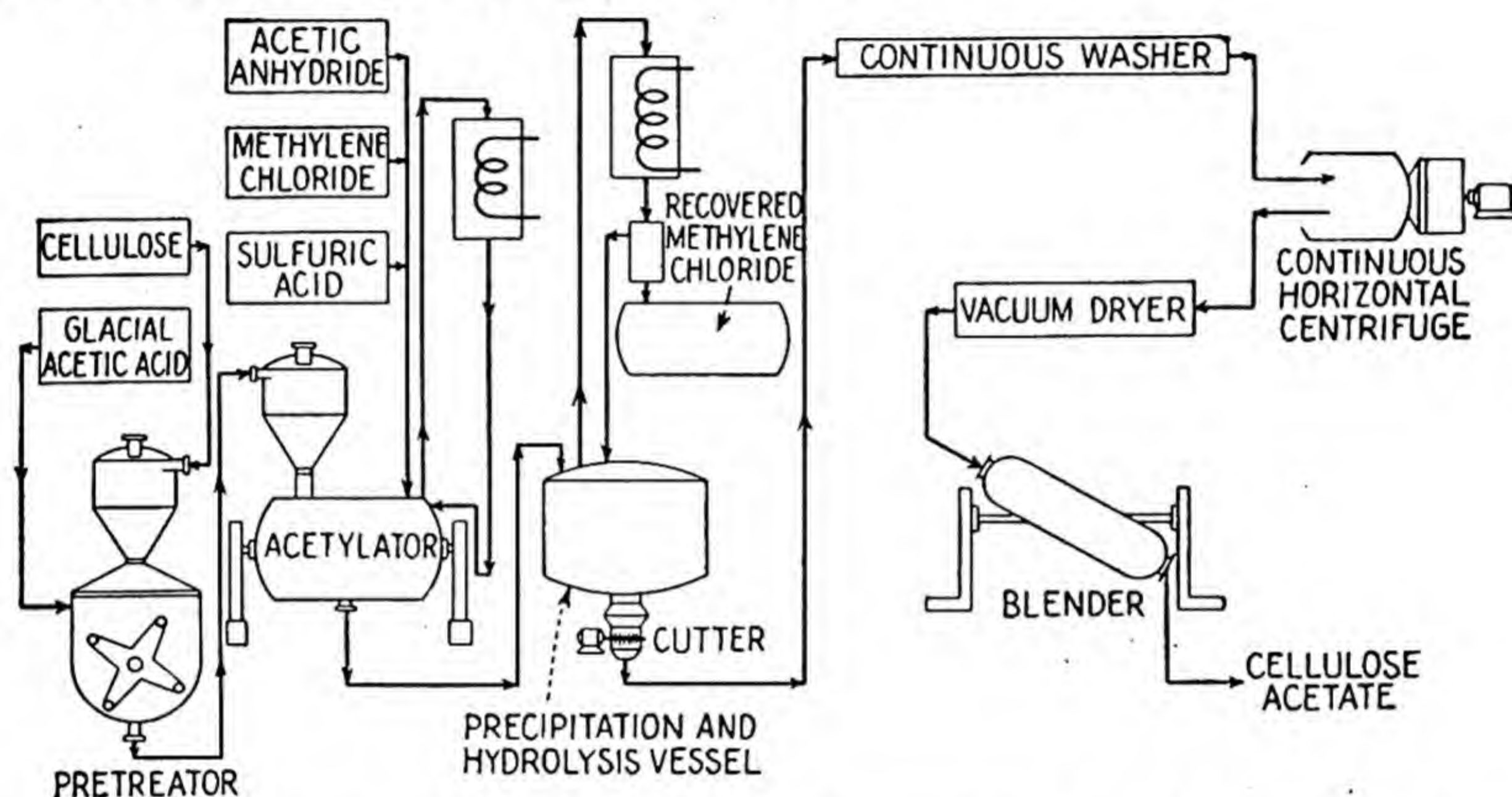
FIG. 59.—Flow sheet for cellulose acetate process employing internal cooling.

Cellulose acetate molding compositions are prepared by mixing precipitated material on heated compounding rolls with plasticizers, dyes, and pigments. The doughy mass after complete mixing is then rolled into sheets or slabs, which are taken from the rolls at specified thicknesses and either blanked out into molding forms or granulated to give molding powder.

Cellulose acetate molding powder is furnished in various granulations with different plasticizers, color, fillers, etc., to suit specific molding requirements and finished material properties. It is available in translucent, transparent, and opaque colors and in mottled and pearl effects and is well adapted to extrusion and injection or compression molding.

As many as 17 grades of acetate molding powders are available, ranging from extra hard to extra soft. In general they are either hard, brittle, and low in impact strength, or soft with high impact strength and a high degree of flow. Cellulose acetate molding blanks are availabe $\frac{5}{32}$ to $1\frac{3}{8}$ in. thick with a maximum area 20 by 25 in.

FEED HOPPER

CIRCULATING WATER APPROX. 70°F.

300°F

370°F.

CIRCULATING HOT OIL

$2\frac{1}{2}''$ DIA. SCREW NOT HEATED
41 R.P.M. APPROX.

35 MESH WIRE SCREEN
AND SUPPORTING PLATE

WATER COOLED SPREADER DEVICE APPROX. 70°F

$5''$ DIA. PULL OUT ROLLS

ELEVATION AT A-A
OF SPREADER DEVICE

ELECTRIC HEATER-7500 WATT JACKET TYPE

440°F.

OUTSIDE AIR RING
AIR TEMP. 200°F

$12\frac{1}{4}''$

$3\frac{1}{4}''$

$\frac{1}{4}''$

A

SPLITTER BLOCK
AIR RINGS-AIR TEMP. 200°F.

$\frac{1}{4}''$ PIPE RING $3\frac{1}{2}''$ DIA

A

$5''$ DIA. PULL OUT ROLLS
STEAM HEATED TO 220°F.

$4''$ DIA. TENSION ROLLS
ROOM TEMPERATURE

29″

7″

CENTER LINE
OF MACHINE

$1\frac{1}{16}''$

4″

$5\frac{1}{2}''$

$\frac{1}{4}''$ PERFORATED COOLING
PIPE-AIR AT APPPROX. 80°F

$1\frac{1}{2}''$ DIA.

TO CUTTER
OR WIND UP

12″ RUBBER CONVEYOR BELT
USE OPTIONAL

DIMENSIONS GIVEN ARE APPROXIMATE   APPROXIMATE OVERALL LENGTH 25 FEET

Fig. 60.—Continuous extrusion machine for producing cellulose acetate sheets.

Sheets of cellulose acetate in various thicknesses are pressed from the original plastic mass. Small sheets of molding blanks are sliced from the thicker sheets and from pressed blocks of the material. Standard sheets are available 20 by 50 in. in maximum size, varying from 0.005 to 1 in. in thickness.

Thin sheets of cellulose acetate having a thickness of 0.010 to 0.040 in. and widths of 10 to 22 in. are made by extrusion. A tube of the desired wall thickness is made $3\frac{5}{16}$ to 7 in. in diameter and slit as it emerges from the orifice rings. Hot air at 105°C. is blown on the slit tube as it passes
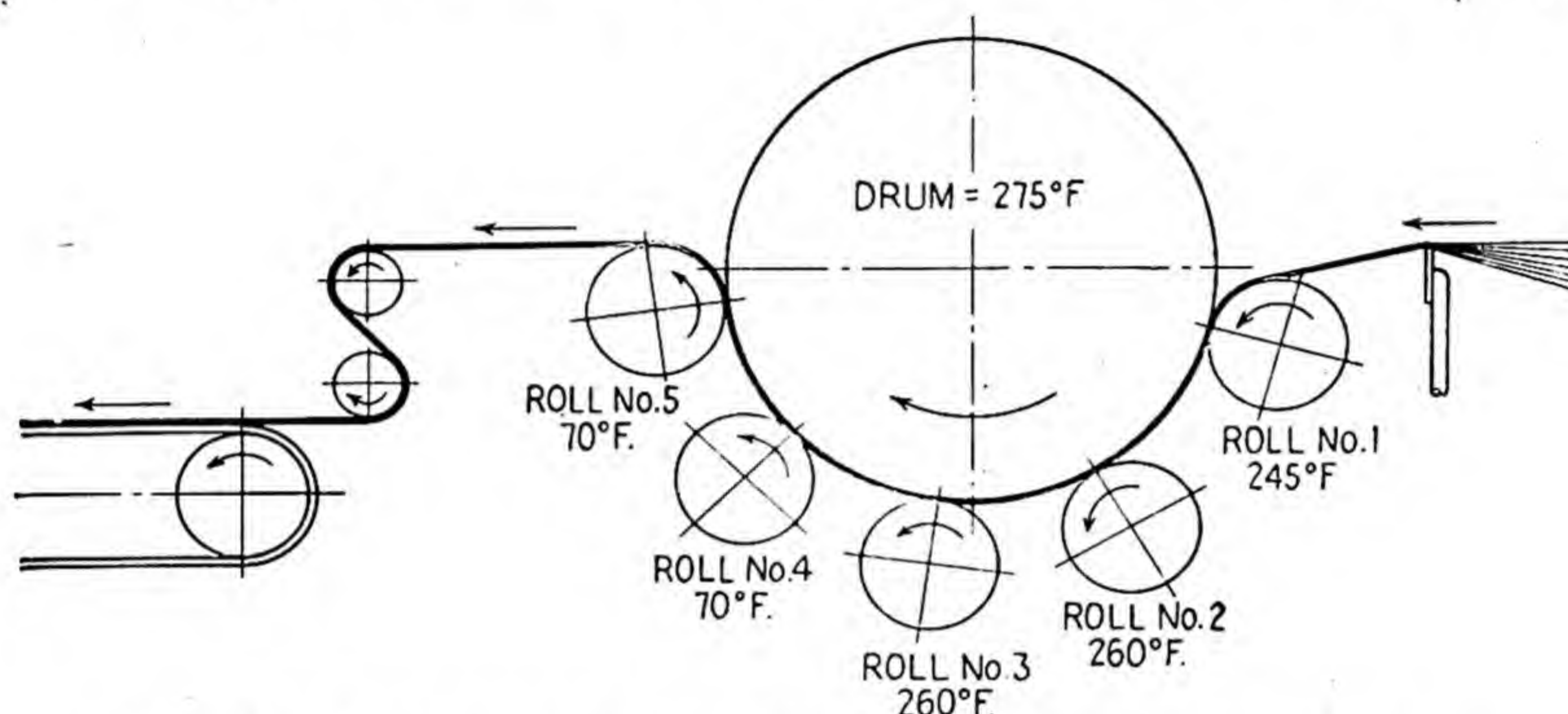
Fig. 61.—Continuous polishing machine for cellulose acetate sheeting.

to a water-cooled spreader which flattens it to a flat sheet. It then passes over pull-out rolls to a pair of tension rolls and onto a belt conveyer. If polishing is desired, the extruded slit sheet passes through a machine consisting of a large heated drum and five equally spaced smaller rolls heated to selected temperatures. Figures 60 and 61 show the extrusion machine and rolls for unpolished and polished sheeting.

Thinner films and foils are made by casting a dope on a polished moving surface. The volatile solvents are evaporated, and the resulting film is stripped from the support, dried, and wound onto rolls. Films 0.005 to 0.010 in. thick may be made by this process.

Cellulose acetate plastic is also extruded hot in the form of rods and tubes and varying profile shapes. They are generally made to customers' specifications. They may range from 0.050 to over 2 in. in diameter; tubes have a minimum wall thickness of about 0.020 in.

Cellulose acetate lacquers are light-resistant and slow burning, have high gloss, hardness, heat resistance, high dielectric strength, toughness, and resistance to mineral oil, alcohol, and gasoline. They may be made into hard and rigid or soft and flexible coatings. The lacquers are used as coatings for wallpaper, textiles, leather, metal foil, protecting containers, sealing bottles, making capsules, insulating tubing, and the like.

Unlike the nitrate, most of the cellulose acetate produced at the present time is used in the manufacture of a textile material. It differs from all the other types of rayon in that it is a cellulose compound and not regenerated cellulose. Many of its properties are dependent on this fact. It is soluble in cellulose acetate solvents, but this fact is not too great a disadvantage since ordinarily there are few opportunities for contact with such solvents. There is, however, one exception to this statement. Liquid fingernail polishes and polish removers contain such solvents. If either of these materials come in contact with cellulose acetate rayon, they will dissolve it. The chief disadvantage of cellulose acetate is its sensi-
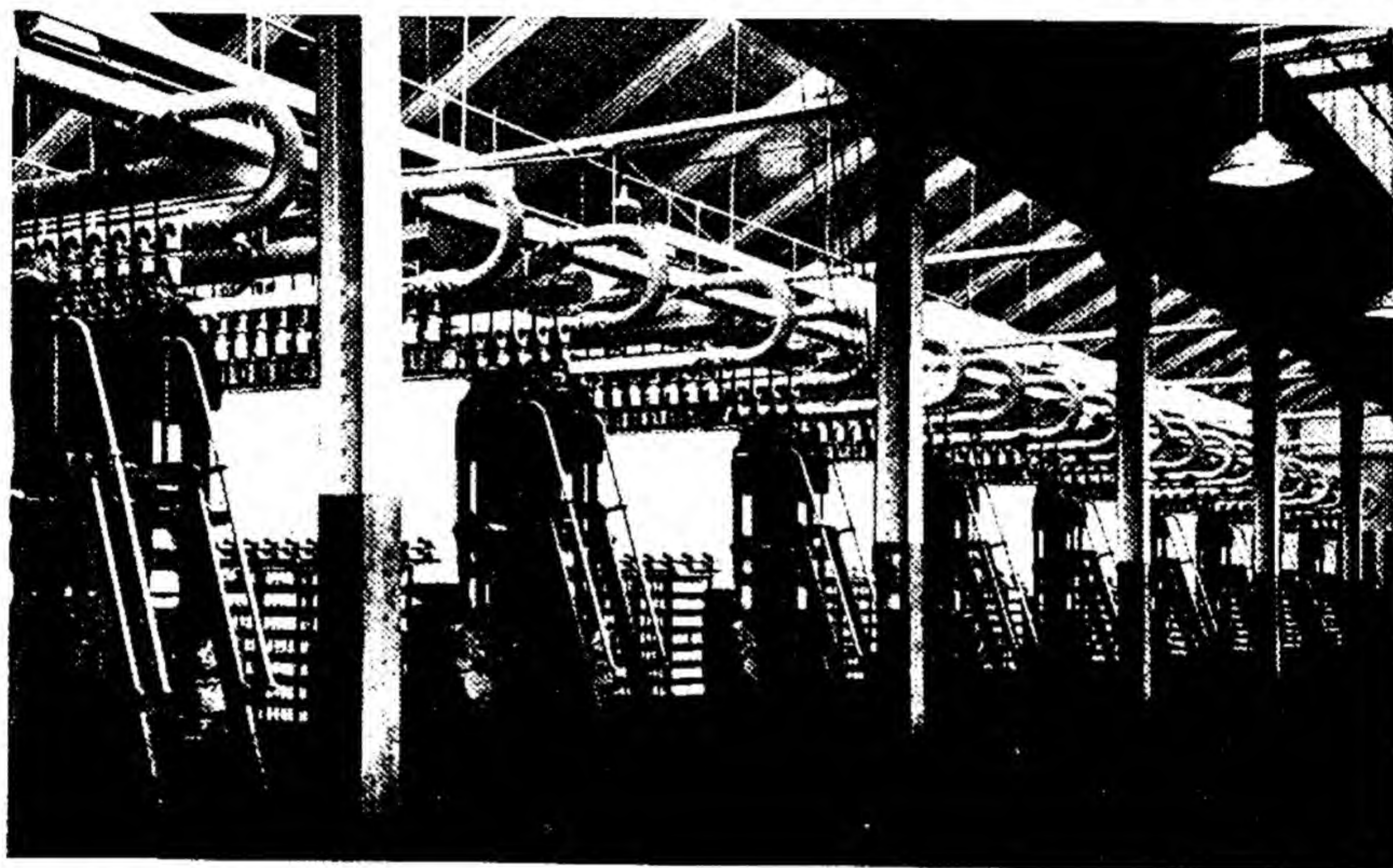
Fig. 62.—A spinning room for the production of cellulose acetate rayon. (*American Viscose Corp.*)

tivity to heat. Acetate materials should not be washed in hot water or subjected to much heat when being pressed. In the early stages of its development it was difficult to dye properly. Special dyes and methods of dyeing have since been developed so that almost all colors and sheens can now be obtained.

The transformation of cellulose acetate into filaments and fibers is accomplished by dissolving the cellulose acetate in acetone, filtering the highly viscous spinning solution, and then forcing it downward through the fine holes of a spinnerette into a rising current of warm air which evaporates the acetone, thus leaving the cellulose acetate in the form of continuous filaments that pass out of the bottom of the spinning chamber and are wound on a bobbin or spool (see Fig. 62). No further chemical treatments or wet treatments are necessary. The yarn is subsequently given the desired number of turns, twisted, and wound onto cones for shipping.

The physical properties of the acetate filament may be varied over rather wide limits.[1] Lustrous filaments are composed of pure cellulose acetate; dull filaments are made by the addition of a small amount of titanium oxide pigment to the spinning solution; black filaments are made by the similar incorporation of carbon black. The size of the filaments and the shape of the cross section may be varied by changing the size and shape of the holes in the spinnerettes. Filaments as fine as silk and filaments or fibers as coarse as carpet wool are available commercially, with a variety of sizes in between.

Cellulose acetate rayon yarn is made in grades varying in number of filaments from 11 to 104 and from 45 to 300 denier. However, most of it is sold in 14- to 68-filament and 55- to 200-denier grades. The denier is the weight in grams of 9,000 m. of yarn. As is indicated in the section under filaments, there is a large amount being manufactured as cut staple.

Coughlin classifies the distinctive properties that characterize the acetate rayons as follows:

1. *Suppleness and Hand.*—Acetate filaments have a softness to the touch and a suppleness that results in exceptional draping qualities and a pleasant feeling against the skin.

2. *Natural Crease Resistance.*—The nature of cellulose acetate results in a degree of elasticity or resilience in the filaments that gives acetate fabrics a marked resistance to wrinkling and creasing.

3. *Low Moisture Absorption.*—Acetate rayon is less hygroscopic than wool, viscose rayon, or silk.

4. *Whiteness.*

5. *Special color effects.*—Special dye requirements often result in unusual and attractive final shades.

<center>PROPERTIES AND USES OF</center>
<center>CELLULOSE ACETATE PLASTICS</center>

Advantages:
    Low flammability
    High impact strength
    Excellent molding properties
    Good electrical properties
    Light weight
    Availability in all colors, transparent, translucent, or opaque
    Low cost

Disadvantages:
    Low softening point (130 to 220°F.)
    Decomposition by strong acids and alkalies
    High water absorption (for a plastic material)
    Limited compatibility

[1] COUGHLIN, W. E., 1944 Plastics Catalog, p. 852.

Common uses:
    Airplane windshields
    Automobile steering wheels
    Costume jewelry and ornaments
    Fountain pens and mechanical pencils
    Goggles
    Instrument and radio panels
    Lamp shades

Cellulose Acetate-butyrate.—Cellulose acetate-butyrate closely resembles cellulose acetate in appearance and uses, so that a complete discussion is not necessary. It is made in the same manner as cellulose acetate, using a mixture of butyric and acetic acids and anhydrides. The properties of the resulting product can be varied by altering the relative proportions of the two acids and anhydrides used, as well as the degree of hydrolysis and the viscosity. In general, the mixed ester has a greater solubility in a wider range of solvents and is compatible with a greater number of plasticizers than is the straight acetate, the moisture absorption is lower, and the impact strength is higher. Molded articles made from cellulose acetate-butyrate have excellent dimensional stability.

A common cellulose acetate-butyrate used in plastics contains about 37 per cent butyryl and 13 per cent acetyl. The following plasticizers are commonly used: dibutyl phthalate, diamyl phthalate, triphenyl phosphate, tricresyl phosphate, dibutoxyethyl phthalate, dibutyl sebacate. A much smaller quantity of plasticizer is required with cellulose mixed esters than with cellulose acetate. As the butyryl content is raised, less plasticizer is required, and compatibility with various plasticizers is greater.

Cellulose acetate-butyrate molding compound is available in granular form for injection and compression molding and forming by continuous extrusion and in sheet or blank form for compression molding only. The molding composition is suited to uses where resistance to humidity and exposure to weather is desired. The composition is soluble in a wider range of solvents and is compatible with more gums, resins, and plasticizers than cellulose acetate. The butyrates are exceptionally well suited to dry extrusion, which permits production of various shapes in any desired length.

Cellulose acetate-butyrate has lent itself to a number of new and interesting commercial applications. One use takes advantage of the ability to cast the material with comparative ease. It can be cast by heating it to 380 to 400°C. and pouring it into wooden molds for use in moderate-sized metal-forming tools, such as drop hammers and hydraulic press punches. It possesses considerable advantage over lead for this purpose.

Cellulose acetate-butyrate has also been applied successfully for hot-melt coating of paper and textiles. By incorporation of waxes and resins, coatings are formed with permeabilities approaching that of moistureproof cellophane.

A very recent application of the material is in gel-dipping lacquers. Solvents are used that give fairly clear mobile liquids at around 120°F. but set to a clear firm gel on cooling to room temperatures. Relatively thick coatings result. The process is especially applicable for coating regular shaped articles of metal, wood, or cardboard.

Both the acetate-butyrate and the acetate-propionate are used in the manufacture of safety film for home and hospital use. All amateur or educational films, usually 8 or 16 mm., are of this type. Commercial film is usually cellulose nitrate.

PROPERTY AND USES OF
CELLULOSE ACETATE-BUTYRATE PLASTIC

Advantages:
    Excellent molding properties
    Good weathering properties
    Low moisture adsorption rate
    High impact strength
    Light weight
    Nontracking characteristic
    Availability in all colors, transparent, translucent, or opaque
    Good compatibility
Disadvantages:
    Low softening point (100 to 180°F.)
    Low flexural strength
Common uses:
    Automobile hardware
    Brush handles
    Radio dials
    Refrigerator hardware
    Costume jewelry and ornaments
    Moving-picture film

Cellulose Propionate.—Cellulose propionate is one of the newer additions to the thermoplastic molding compositions. Its manufacture is very similar to that of the cellulose acetate material, being a partly hydrolyzed product. In amount of plasticizer required to obtain equivalent flows in the molded product, it lies between the acetate and acetate-butyrate types.

Although the properties of cellulose propionate have been known for many years, its commercial exploitation has been delayed by the unavailability of propionic acid in quantity and at a sufficiently low price. Recently, new synthetic processes for the production of the acid have been developed.

In the manufacture of the ester, the same method and type of equipment is employed as in the case of the cellulose acetate and acetate-butyrate types.

Ethyl Cellulose.—Ethyl cellulose is a cellulose ether in which ethyl groups have replaced the hydrogens in the hydroxyl groups of the glucose residues.

The standard ethyl cellulose available commercially has been substituted to the extent of 2.4 to 2.5 ethoxyl groups per glucose residue.

The first step in the preparation of ethyl cellulose is the formation of alkali cellulose. Linters or pulp are shredded to produce thin narrow aggregates of loosely felted fibers. These fibers are conveyed to a trough in which they are moistened with a spray of caustic. The wetted material is then conveyed to the reactors. Ethyl chloride and excess caustic are also added to the reactors. After the reactors have been charged, the temperature is raised to 350 to 400°F. and the reaction allowed to continue for a controlled length of time. By control of temperature, pressure, reaction time, and ratios of raw materials, it is possible to control the ethoxyl content and the viscosity of the product.

When the reaction is completed, the ether and alcohol that are formed as by-products by the action of the caustic on ethyl chloride are flashed off, the vapors scrubbed with sulfuric acid, and the solvents condensed and recovered. As the solvents are removed from the reactors, ethyl cellulose precipitates in a liquor consisting of excess caustic and salt. This slurry is blown to wash tubs in which the caustic is drained off and the ethyl cellulose is given a preliminary washing (see Fig. 63).

The rather large granules of ethyl cellulose are then dropped into disintegrators where they are ground to a uniform size. This grinding makes it possible to remove additional salt and caustic by an additional wash and stabilizing treatment. Excess water is then removed in a centrifugal, and the product is dried, blended, and stored according to grade.

Ethyl cellulose containing 2.4 to 2.5 ethoxyl groups (47 to 48 per cent ethoxyl content) possesses the widest variety of useful properties. The property of unusual toughness is coupled with thermoplasticity and low flammability. It burns about like cellulose acetate. The unplasticized material is flexible at temperatures as low as −40°C., and it is fairly extensible. Because of these facts, ethyl cellulose compositions possess a high degree of low-temperature toughness. The maximum advantage can be realized from the thermoplastic character of ethyl cellulose because it is also stable to heat. It is inert to alkalies of all strengths and has excellent solubility and compatibility with a wide variety of solvents, resins, waxes, oils, and plasticizers. Moisture absorption is about 2 per cent, which is somewhat better than cellulose acetate and slightly poorer than cellulose nitrate.

Ethyl cellulose has a specific gravity of 1.14 in comparison with 1.32 for cellulose acetate and 1.47 for cellulose nitrate. This low value is an advantage since ethyl cellulose is sold on a pound basis and frequently molded into objects where the amount required is determined by the volume of the articles produced.

Straight-chain petroleum hydrocarbons comprise the only class of organic liquids that do not exhibit marked solvent action on ethyl cellulose. The
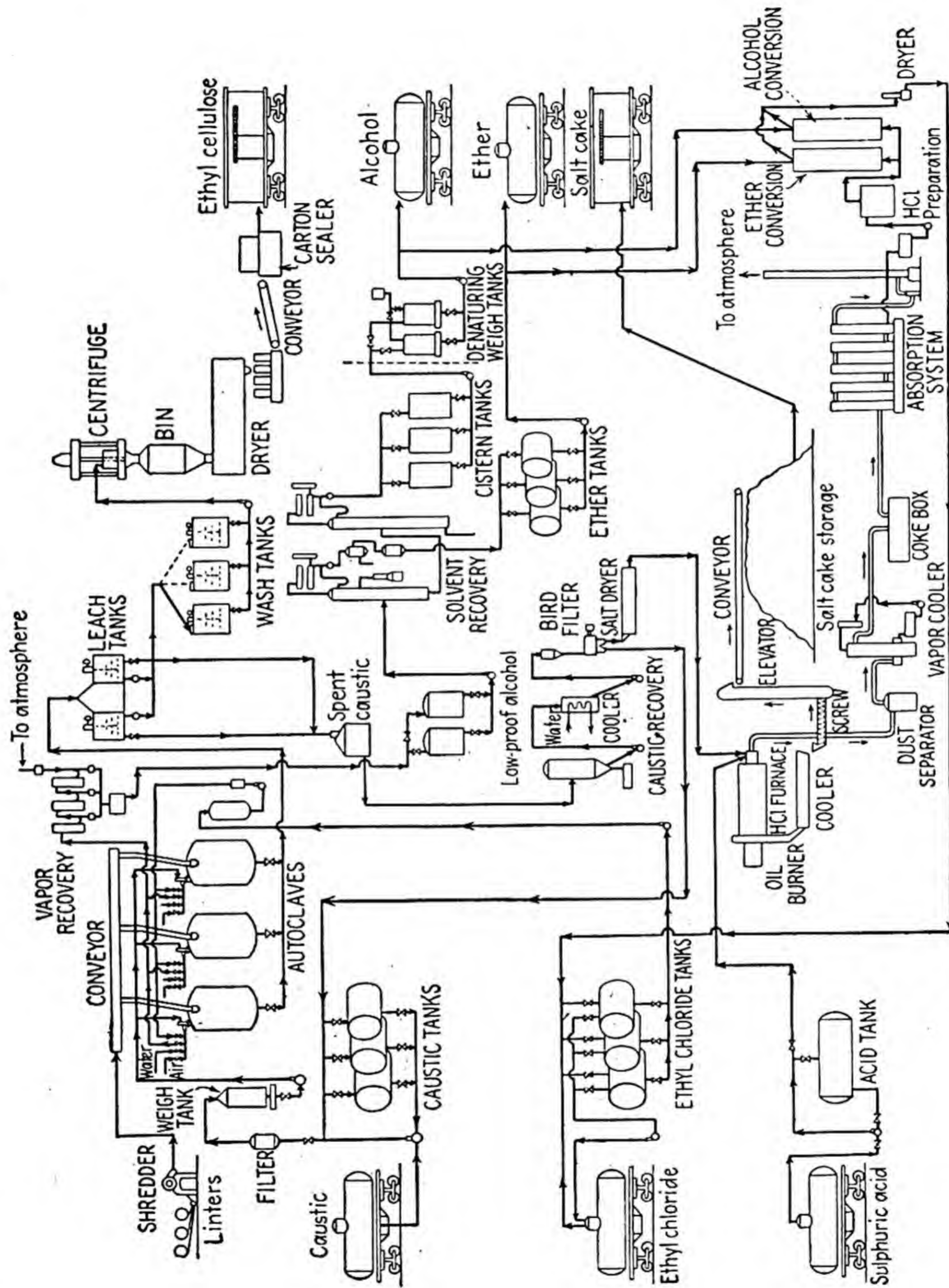
Fig. 63.—Flow sheet for ethyl cellulose. (*Chem. and Met.*)

available plasticizing agents are numerous and cover such widely divergent classes as high-boiling esters, raw oils, air-blown oils, fatty acids, and chlorinated diphenyl derivatives. Compatible resin classes include natural resins, phenolics, rosin-modified maleates, alkyd resins and ester gum; but ethyl cellulose is not compatible with polystrene, polyvinyl esters, or paraffin wax. Ethyl cellulose dissolves readily in hot resins, oil, waxes, platicizers, and mixtures of these in the absence of any volatile solvent. These compositions can be applied as molten mixtures at elevated temperatures and form the bases for some adhesives and coatings.

The mechanical properties of ethyl cellulose are exceptionally good over a wide range of temperatures and humidity conditions. Its electrical insulating properties are satisfactory for many purposes, particularly where its property of retaining high flexibility at low. temperatures is important. This property is also important where gaskets and fabricated materials are exposed to extremely low temperatures that would cause most resins to become brittle.

One of the most important applications of ethyl cellulose is its use with other resins in lacquers, varnishes, and adhesives to improve toughness and flexibility. It is added to waxes to increase strength and melting point. A wide variety of films and foils are made for general use. Molded objects of all sorts, fabric coatings, insulation, and extruded tubing are made from ethyl cellulose compositions. It is widely used for the strip-coating method of protecting machined parts or for outdoor protection of airplanes and ordnance.

PROPERTIES AND USES
OF ETHYL CELLULOSE PLASTIC

Advantages:
Good heat and light stability
Good electrical insulating properties
High impact strength and toughness
Good caustic resistance
Good moldability
Availability in all colors
High flexibility at low temperature

1. isadvantages:
High water absorption
Tendency to cold flow
Low softening point (110 to 200°F.)
Attacked by most organic solvents

Common uses:
Automotive parts
Costume jewelry
Electrical appliances
Insulation
Radio cabinets
Rigid boxes and containers
Special waxes

Methyl Cellulose.—Methyl cellulose is prepared by a process almost identical with that for ethyl cellulose, substituting methyl chloride or sulfate for the corresponding ethyl derivative. Trimethyl cellulose is not readily obtained by this method, but the partly methylated derivative has the most useful properties so that the completely methylated compound is not desired.

The most widely used grades of methyl cellulose contain 25 to 30 per cent methoxyl and are water-soluble. They are more soluble in cold water than in hot so that solutions become more viscous and finally gel as the temperature is raised. Water solubility plus the ability to produce viscous solutions has made methyl cellulose useful as a thickening agent in the textile, food, and adhesives industries. Since it is edible, it can be used as a base for salad dressings and other thickened food products.

It is also useful as an emulsifying and dispersing agent in the textile, cosmetic, and paint industries and has been used as a grease-proof paper size and coating.

Oxidixed Cellulose.—An interesting product that has been introduced to the trade quite recently is oxidixed cellulose. It is produced by controlled oxidation of cellulose with nitrogen tetroxide which has the property of selectively acting on the primary- hydroxyl groups of cellulose, converting them to carboxyl groups. It is represented by the following unit structural formula:
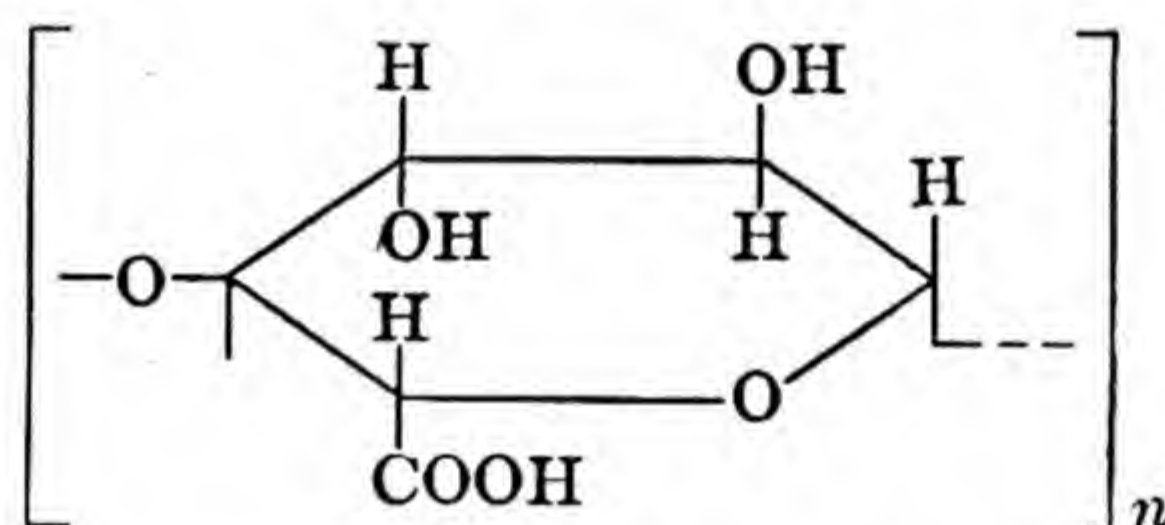
It is obtained upon complete oxidation of all primary hydroxyl groups and is called "polyanhydroglucuronic acid" and corresponds to a carboxyl content of 25.5 per cent. However, the product made for the trade contains 15 to 20 per cent carboxyl and corresponds to a copolymer of anhydroglucuronic acid and anhydroglucose units.

The product has the properties that would be predicted from its structure. It is a moderately strong acid, is soluble in weak alkali solutions at room temperature, and forms insoluble salts with alkaline earths. It is insoluble in common organic solvents. The oxidized cellulose is a high polymer, but is considerably degraded as compared with the original cellulose.

Oxidized cellulose has found use as surgical gauze and bandages, where use is made of its solubility in the alkaline fluids of the body.

Alginates.—Algin is a natural high polymer extracted from a type of seaweed. The laminariae species of brown algae is deposited by the tide

on European shores. When extracted with alkali, sodium alginate is obtained. It is the sodium salt of d-mannuronic acid, a colloidal polysaccharide $(NaC_6H_7O_6)_n$. Sodium alginate is a hydrophobic colloid and has found use in ice cream, jellies, marshmallows, and pudding powders. It can also be made into glues and adhesives. The calcium salt is used for waterproofing concrete and fireproofing wallboard.

Considerable development work has been carried out in England on the use of alginic acid as a textile fiber. When the purified alkaline extract is spun into a coagulating bath containing calcium chloride, hydrochloric acid, and olive oil, a rayon satisfactory in appearance and strength can be obtained. The fiber is resistant to boiling water and acids and is nonflammable.

Although the use of the alginates in textiles is still in its infancy, it seems possible that this high polymeric material may become a factor in the industry.

RUBBER DERIVATIVES

Chlorinated Rubber.—Chlorinated rubber was first prepared in the middle of the nineteenth century, but it was not until 1917 that a commercial method of chlorinating a 4 per cent solution of rubber in carbon tetrachloride was developed. Since crude rubber is composed of long chains of isoprene units in which there is one double bond, it should give a product to which has been added two chlorine atoms.

$$\left[-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-\right]_n \xrightarrow{Cl_2} \left[-CH_2-\underset{\underset{CH_3}{|}}{CCl}-CHCl-CH_2-\right]_n$$
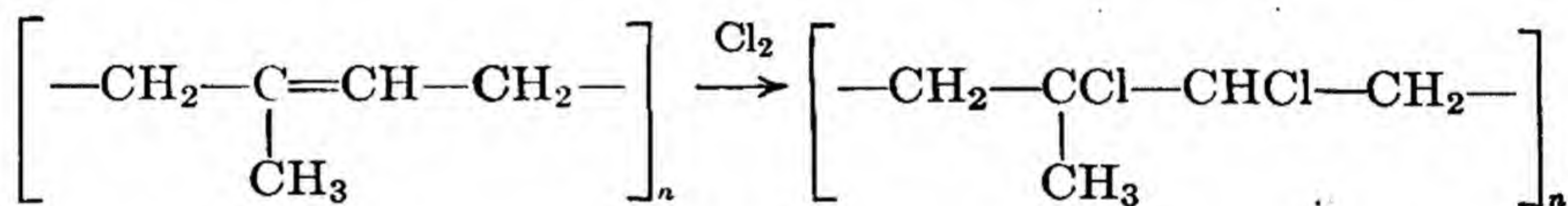
However, this compound contains only 51 per cent chlorine, whereas the commercial product will average 66 to 68 per cent. In addition, considerable hydrogen chloride is given off, indicating that substitution was occurring as well as addition. The final product contains three to four chlorine atoms for each isoprene unit.

Crepe rubber is first worked on rolls to reduce the viscosity and then put into solution in carbon tetrachloride in glass-lined kettles. Chlorine is bubbled through this solution and reacts with the rubber to form the chlorinated product. Reflux condensers are used to retain the carbon tetrachloride, while hydrochloric acid and some excess chlorine pass over to tantalum absorbers where the acid is recovered (see Fig. 64).

When the chlorination operation is completed, the solution flows down into chemical brick-lined steel storage tanks. From these tanks it is pumped into brick-lined precipitating tanks that are full of hot water. The solvent and steam are condensed, passed through a separator, and the

carbon tetrachloride returned to storage for reuse. The granular precipitate is centrifuged, washed, dried, and packaged.
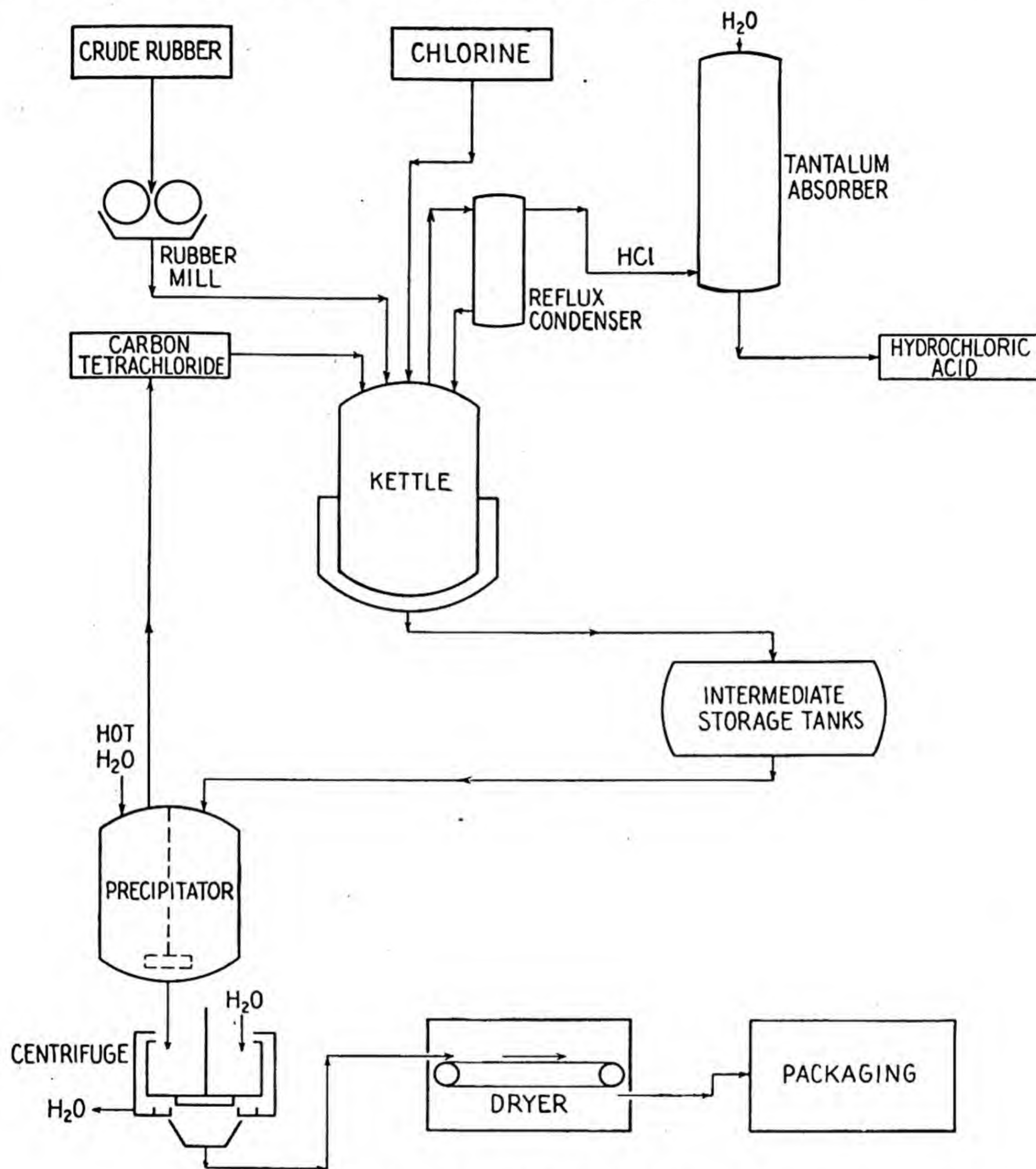
FIG. 64.—Flow sheet for chlorinated rubber.

Chlorinated rubber is marketed as a white granular powder in four viscosity grades. Viscosities are determined in a 20 per cent solution in toluene at 25°C., and the general uses recommended are as follows:

5 centipoise..........For printing inks and where maximum solids or maximum fluidity is desired

10 centipoise..........For high solids chlorinated rubber lacquer type coatings and as a fortifying agent for alkyd enamels and oleoresinous varnishes

20 centipoise.........For general protective coating applications; also as a fortifying agent, as above

125 centipoise.........For concrete floor paints, paper lacquers, adhesives, textile coatings and other applications requiring maximum mechanical strength

Solubility goes up as lower viscosities are used, and the material becomes compatible with wider ranges of resins and plasticizers. On the other hand, as higher viscosities are used, flexibility and mechanical strength are improved. Therefore, the viscosity selected for any given use will represent a compromise according to the properties desired.

Chlorinated rubber coatings are unaffected by 50 per cent sodium hydroxide, 45 per cent nitric acid, and the strongest bleaches. Much more important, however, is the undisturbed surface obtained in the face of such common chemically destructive agents as simple dampness, seepage moisture, soaps, cleaning compounds, vapors and fumes of various kinds, mold and mildew, mineral oils, cement alkali, and plaster lime. Second only to chemical resistance is rapid drying—a drying speed that in paints, synthetic enamels, and printing inks can generally cut drying times one half or more.

Chlorinated rubber possesses one of the highest degrees of water impermeability and one of the lowest degrees of water absorption (0.27 per cent absorption at 80 per cent relative humidity in 24 hr.) of the various coating materials. In addition it is odorless, tasteless, nontoxic, and nonflammable.

PROPERTIES AND USES
OF CHLORINATED RUBBER

Advantages:
   Resistance to moisture
   Resistance to chemicals
   Quick-drying coatings
   Nonflammable
Disadvantages:
   Thermoplasticity—not good at elevated temperatures
   Solubility in aromatic solvents
   Low resistance to fats
   Low compatibility
Common uses:
   Coatings for
   Corrosive conditions
   Damp conditions
   To resist soaps and chemicals
   Cement
   Tanks, etc.

Rubber Hydrochloride.—Another derivative of rubber that has attained importance as a film-forming substance is rubber hydrochloride. This derivative is prepared by reacting natural rubber with hydrochloric acid.

The hydrogen chloride adds to the double bond in each of the isoprene units in the rubber.

$$
\left[\ -CH_2-CH=C-CH_2- \atop CH_3 \right]_n + HCl \longrightarrow \left[\ -CH_2-CH_2-\overset{Cl}{\underset{CH_3}{C}}-CH_2- \right]_n
$$
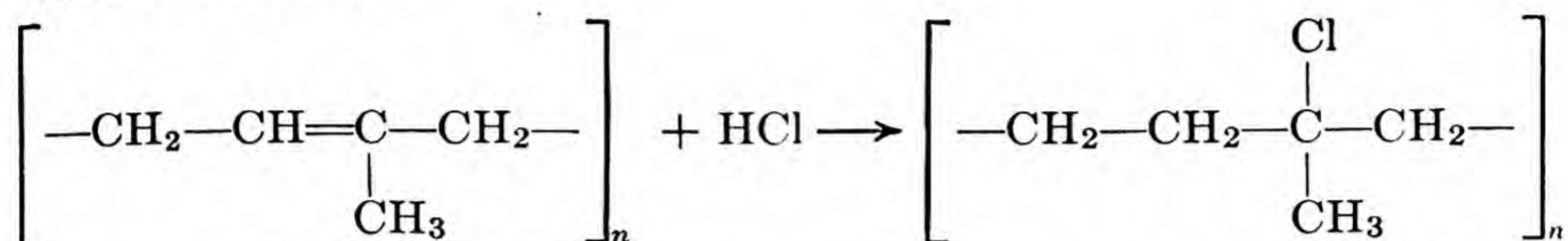
Two methods are available to carry out this reaction. In one, hydrogen chloride gas is bubbled through a solution of rubber in naphtha, benzene, or a chlorinated hydrocarbon. The product is precipitated from solution by alcohol, neutralized with an alkali such as ammonia or sodium carbonate, washed, and dried. It then exists as a white powder. The second method consists of treating crepe rubber directly with liquid hydrogen chloride at temperatures of −15 to −50°C. In both methods the reaction is stopped at about 88 per cent of complete hydrochlorination, since the fully reacted product is brittle. At this point it contains approximately 30 per cent chlorine.

Films are produced by dissolving the hydrochloride in a suitable solvent to form a casting solution. The casting solution is extruded onto a rubber belt coated with water-soluble resin. Just before completing one revolution on the belt, the film is stripped off, returned through a drying compartment, and wound up at the foot end of the machine. The extra passage through the drier removes the last traces of solvent retained in the film.

The film possesses a high elongation and good tear resistance so that it can be sewed or stapled like cloth or paper. Since it softens at 110 to 120°C., it can be welded easily by the application of heat and mild pressure. This method is used to seal seams and edges by continuous rolling heated wheels or knife-edges. Two other characteristics are relatively unusual in the film. It is resistant to the passage of water vapor, and it can withstand considerable deformation, after mild heating, to permit so-called "stretch wrapping" of very irregular objects.

The permeability of rubber hydrochloride films varies from 10 to 20 g. of water vapor per square meter per 24 hr., a value that is approximately optimum for the packaging of machine parts to protect them during shipment. Whole airplane engines are packaged in this material and then crated for shipment. Bags of silica gel are placed inside the film envelope to adsorb the small amount of water passing through the film. This method of protection does away with the grease coating that takes so long to remove and saves approximately 200 man-hours in putting the engine into service.

. Its inertness and ease of fabrication have made it important in the field of food packaging and protection. It is effective in the odor protection of

foodstuffs in home ice boxes and has even been used as the only container for such things as tomatoes.

Rubber hydrochloride films have been used as raincoats and umbrellas, but its low tear resistance is a disadvantage in this application. It is, however, an excellent garment cover. Other applications are shower curtains and bottle-cap liners.

CASEIN AND OTHER PROTEIN PLASTICS

Casein plastic materials were originally introduced in Germany during the year of 1900. They were given the trade name Galalith (milkstone), and this term spread to the United States as a general term for casein plastics. In comparison to the flammable cellulose nitrate and dark-colored phenolic resins, Galalith had the advantages of being nonflammable and light colored. Its weaknesses included a long process of manufacture, limit in form of primary products to sheets and rods, and high water absorption. The properties of nonflammability and light color were distinct advantages over existing competing materials; so this plastic was produced in quantity and adapted to many uses.

When casein plastics were introduced in the United States in the early twenties, it was soon found that climatic conditions here made its utilization impractical, and the development of cellulose acetate, urea-formaldehyde, and vinyl resins soon restricted its use to the production of buttons and other small objects.

Research on casein revealed that casein hardened by treatment with alum became stiff enough to permit it to be worked on automatic screw machines for the production of small objects. The turnings of alum-hardened casein can also be reworked. Since the button industry utilizes special types of automatic screw and stamping machines, a logical development was the combination of casein manufacture with button factories. These developments form the basis of the industry as it exists today. Only one company produces casein plastic sheets and rods, but several button companies produce finished buttons and simple buckles directly from casein, consuming in the process about 5,000 tons of casein annually in normal times. This industry, coupled with the recently expanded use of casein for fiber production, consumes practically all the casein utilized in the field of plastics.

The process by which sheets and rods of casein plastic material may be produced consists of wetting the powdered rennet casein to a water content of 30 to 40 per cent, converting it to soft plastic, and extruding it from screw-type extruders as rods. Sheets and rods are hardened by immersion in 4 to 5 per cent formaldehyde solution. After seasoning or drying the products to normal moisture content (about 12 per cent) and straightening

them, they are ready for use. The hardening and seasoning processes require weeks to months, depending upon the thickness of sheets and diameter of rods. A 1 in. rod will require a period of almost 1 year.

The process at present employed (see Fig. 65) in the direct manufacture of buttons and buckles from casein consists of adding to the prepared mixture of casein, water, and coloring material about 2 per cent of alum
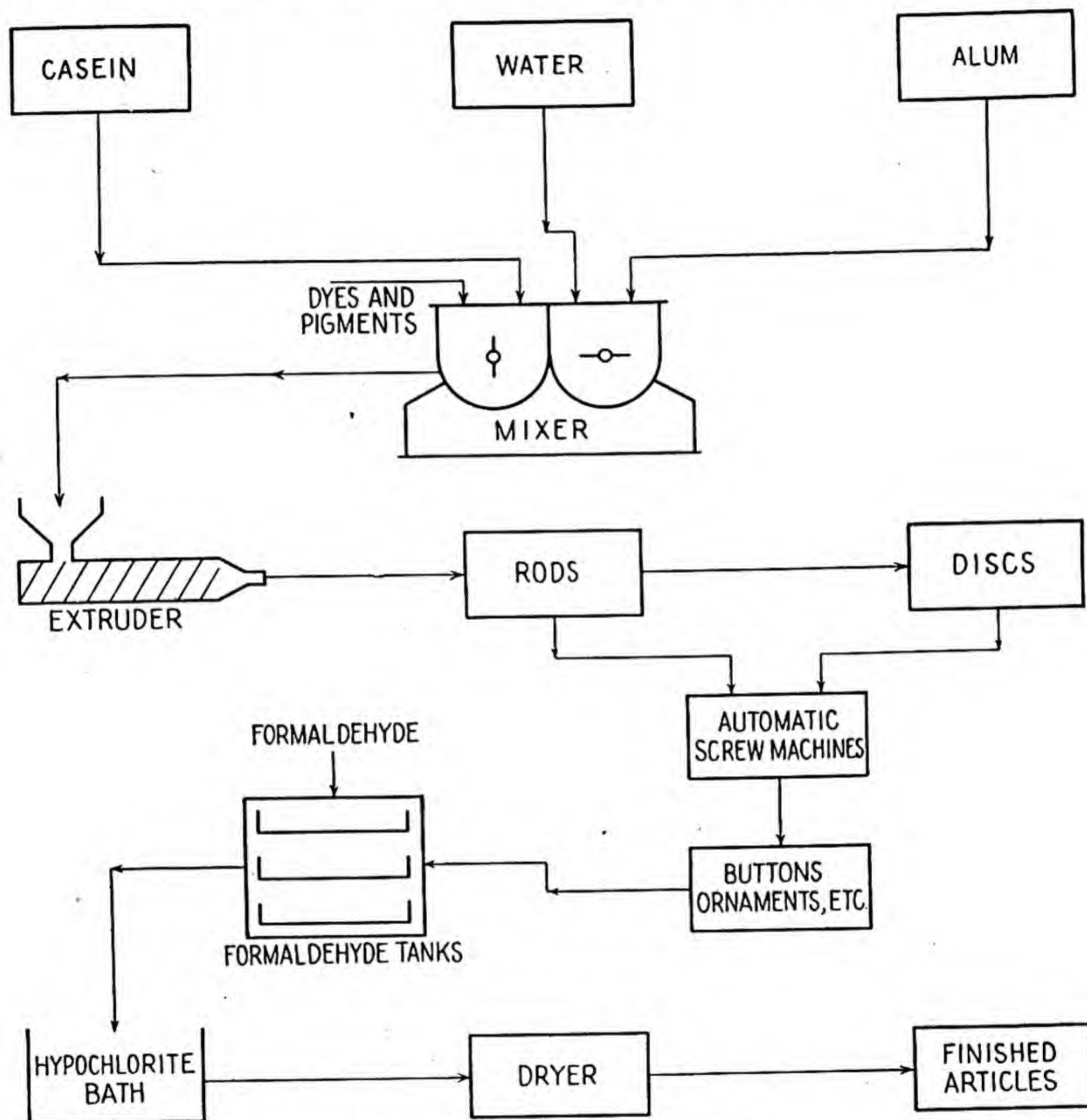
FIG. 65.—Flow sheet for casein.

and extruding the rods of alum-casein. The rods are either placed directly in automatic screw machines, which turn out the buttons in essentially their final shapes, or sliced into disk-shaped blanks, which are turned into button forms in automatic machines. The button forms are hardened in 4 to 5 per cent formaldehyde solution, and, because they are quite thin, the hardening process requires only a few days. They are then drilled in automatic machines and are finally subjected to a chemical or mechanical treatment to develop a glaze or polish on the surface. For

buckles, the plastic is extruded in the form of a ribbon, from which the buckles are punched.

The polish on articles made of casein plastic may be obtained by buffing, but it is usually obtained by dipping in a hypochlorite bath. After 2 to 5 min., the articles are removed from the bath, rinsed with water, and dried. The surface is soft when removed from the bath, but sets to a glaze upon drying.

Protein plastic compositions are hygroscopic and are accordingly affected by atmospheric moisture changes. The absorption of water causes severe warping in sizes larger than 4 sq. in. The soft uncured plastic may be molded to shape, but the molded shapes require hardening in formaldehyde solution, and since thinner sections harden sooner than the thicker parts, the resulting internal stresses and strains would cause severe warping.

The wide range of colors possible in casein plastics was one of the chief reasons for its commercial development, and, although other newer resins possess similar colorability, it still is an important advantage. Protein is an excellent base for taking acid dyestuffs, and the light straw color of rennet casein makes possible the production of material in all shades of color, including the most delicate pastels, all of which take an excellent polish. Casein plastic can be readily machined, but the hardened material dulls cutting edges rapidly. This difficulty is avoided if objects are formed from alum casein and then hardened and polished.

Textile Fiber from Casein.—A casein fiber is being manufactured in the United States at the rate of several million pounds a year. It is used as a textile fiber in a manner similar to rayon and is blended with rabbit fur in making hats. Protein fibers have been produced from soybean, peanut, and other proteins by essentially the same process as that employed for casein. In this process, the protein is first dissolved in an alkaline solution and then extruded into an acid coagulating bath containing dissolved salts. After extrusion, the fibers are hardened with formaldehyde.

The casein-fiber industry and large-scale production of similar fibers from other proteins will depend on relative price and relative quality. In spite of marked fluctuations in the price of casein, the fiber has sold for 64 cents a pound for some time. Further improvements in the wet and dry strengths will enhance the competitive position of this class of fibers.

British Patent 483,731, issued to A. Ferretti, covers in detail a process for manufacturing casein fiber. The special textile casein is prepared from skim milk by precipitation with sulfuric acid in 56 per cent excess of the amount ordinarily employed to coagulate the casein. The casein is then heated without separating it from the acid whey at a pH of 2.9 to 3.0 for 1 hr. at 45°C. The curd is separated, pressed, and dried without washing. This special casein is then dissolved in a caustic solution, using a quantity of sodium hydroxide equal to 9.76 g. per 100 g. of moisture-free casein.

This solution contains about 17 per cent casein. After being aged for 48 hr., the solution is spun into a precipitating bath of sodium sulfate, sulfuric acid, and aluminum sulfate (see Fig. 66). The fiber is hardened in a series

FIG. 66.—Spinning casein fibers. (*Aralac, Inc.*)

of solutions containing sodium chloride and formaldehyde, washed, and dried.

The finished fiber is white to light tan in color with medium luster. It has a warm soft feeling, natural crimp, and a high degree of resilience and flexibility. The tensile strength of protein fiber is about 80 per cent as compared with wool, whereas its dry elongation of 40 per cent and wet elongation of 60 per cent are much higher. Tensile strength at breaking is approximately the same dry and wet, but the point of yielding is lower when wet. The fiber is nearly circular and has little pigmentation.

PART IV

RESINS FORMED BY CONDENSATION REACTIONS

The resins in this class form an important part of the total production of all resins both because of the large tonnage produced and the wide variations in their properties and uses. Over 350 million pounds of these resins was produced in the United States in 1945. The types available vary all the way from laboratory curiosities to the phenolic molding powders that have been the standard general purpose molding powders for the molding industry for the past 30 years.

The commercial development of the phenol-formaldehyde resins, starting with patents issued in 1907, is considered to be the beginning of the truly synthetic molding materials. The development of the alkyd type of polyester and the adaptation of phenolic resins in the paint and varnish industry has had a similar important effect on coatings in general. Likewise, nylon is rapidly assuming a major role in textiles. These developments, in some respects at least, form the solid foundation on which the plastics industry rests. Constant research has brought about new modifications, adaptations, and improvements of the older types of resins, and many variations now in the hands of the research laboratories are only awaiting cheaper methods of obtaining raw materials or uses that would justify their adaptation before becoming commercial products.

With a few relatively minor exceptions, this class of resins includes all the thermosetting materials. These resins have a heat resistance and general easy adaptation to production molding methods not characteristic of any other class of resins.

PHENOL-ALDEHYDE RESINS

Phenol-formaldehyde resins were discovered as early as 1872, but successful commercial application was not made until Baekeland took out his first patents in 1907. This date marked the start of the modern synthetic-resin industry, although cellulose nitrate had been known and used for some time. The nitrate was somewhat of a curiosity, and most of its applications were made to capitalize on this fact. With the development of Bakelite, however, many new fields and applications were developed. Shortly after Baekeland's first patents, other patents were secured by the Condesite and Redmanol companies. Long-drawn-out lawsuits were started and finally resulted in a consolidation, making the Bakelite Corporation the only producer until the patents ran out in 1926.

The reaction is essentially a condensation between phenol, or a mixture of cresols, and formaldehyde. The initial reaction, using an alkaline catalyst, produces hydroxybenzyl alcohols called "saligenols."
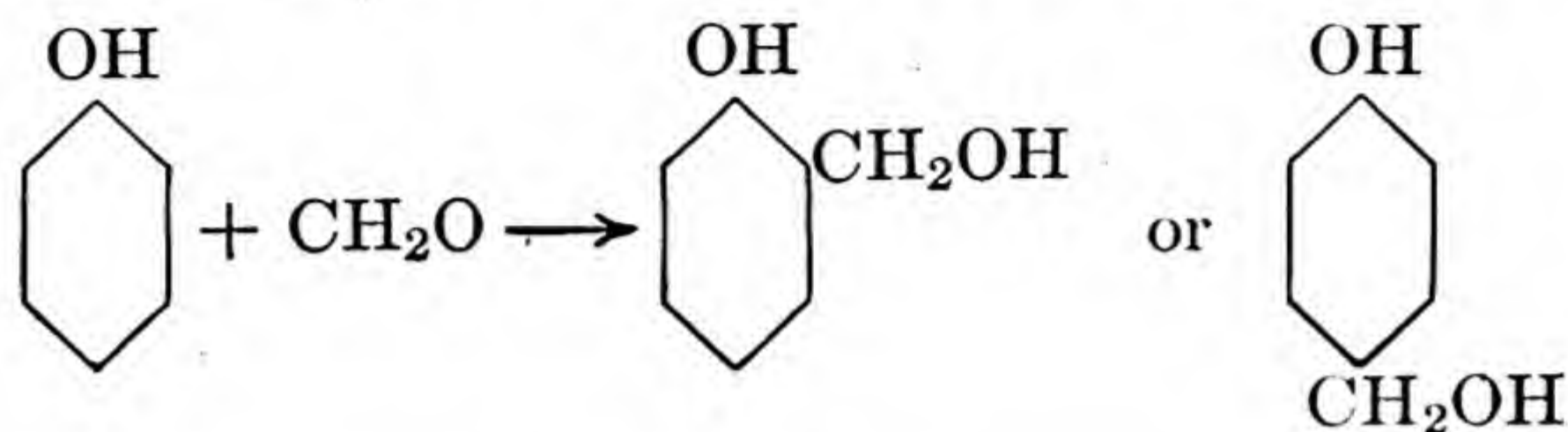
Simultaneously, additional formaldehyde may react to give both di- and trimethylol phenols.
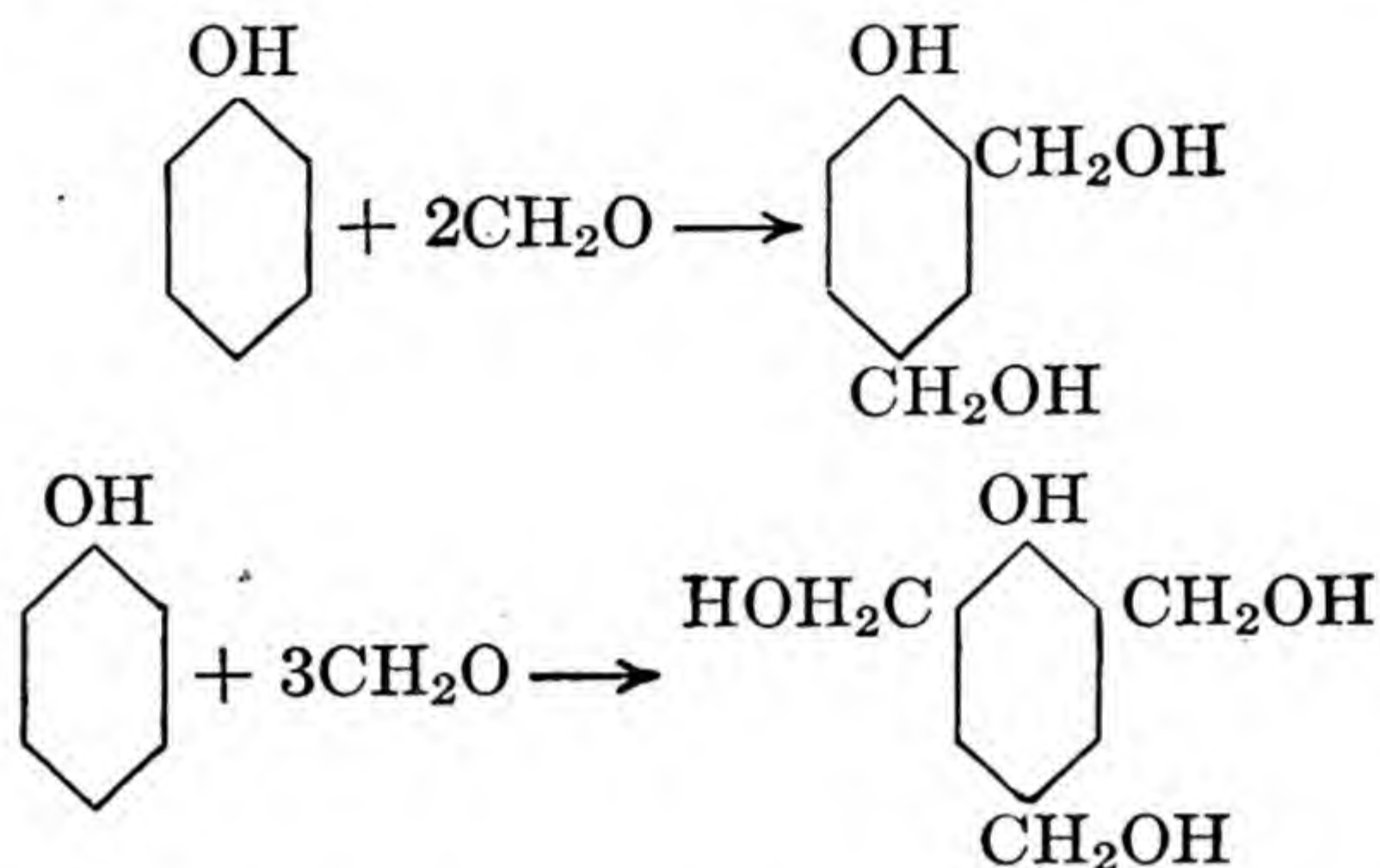
These alcohols continue to condense and polymerize with each other rapidly and almost violently. Part of this reaction is undoubtedly the formation of a linear polymer as follows:
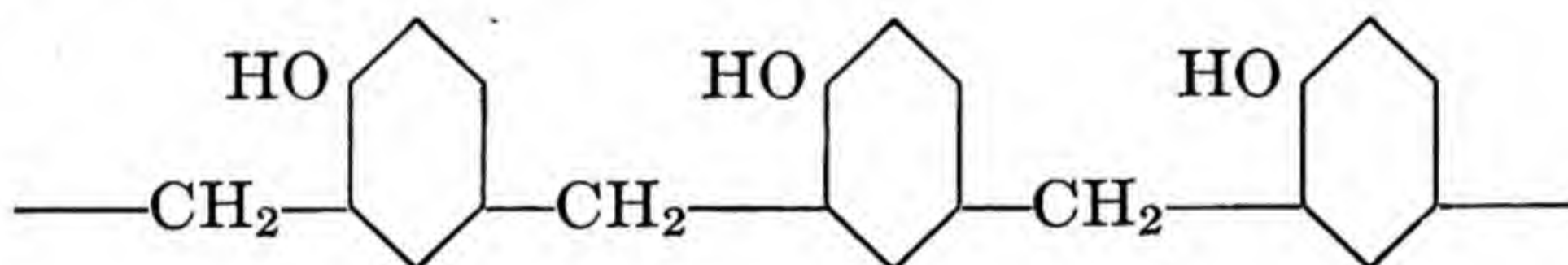
If an acid catalyst is used and the molar ratio of phenol to formaldehyde is greater than one, the reaction stops at this point. It should be realized that di- and trialcohols are formed and undoubtedly enter into the formation of the straight chains. This structure is that of a typical linear polymer and, as such, has thermoplastic properties in that it is soluble and fusible. Additional formaldehyde or hexamethylene tetramine is added to form cross linkages between the chains and thus convert it into a thermosetting three-dimensional structure.

The exact number and positions of the cross linkages in various grades of phenol-formaldehyde resins are not known, but it is possible to postulate a very complex highly idealized three-dimensional structure if the ratio of phenol to formaldehyde is correct.
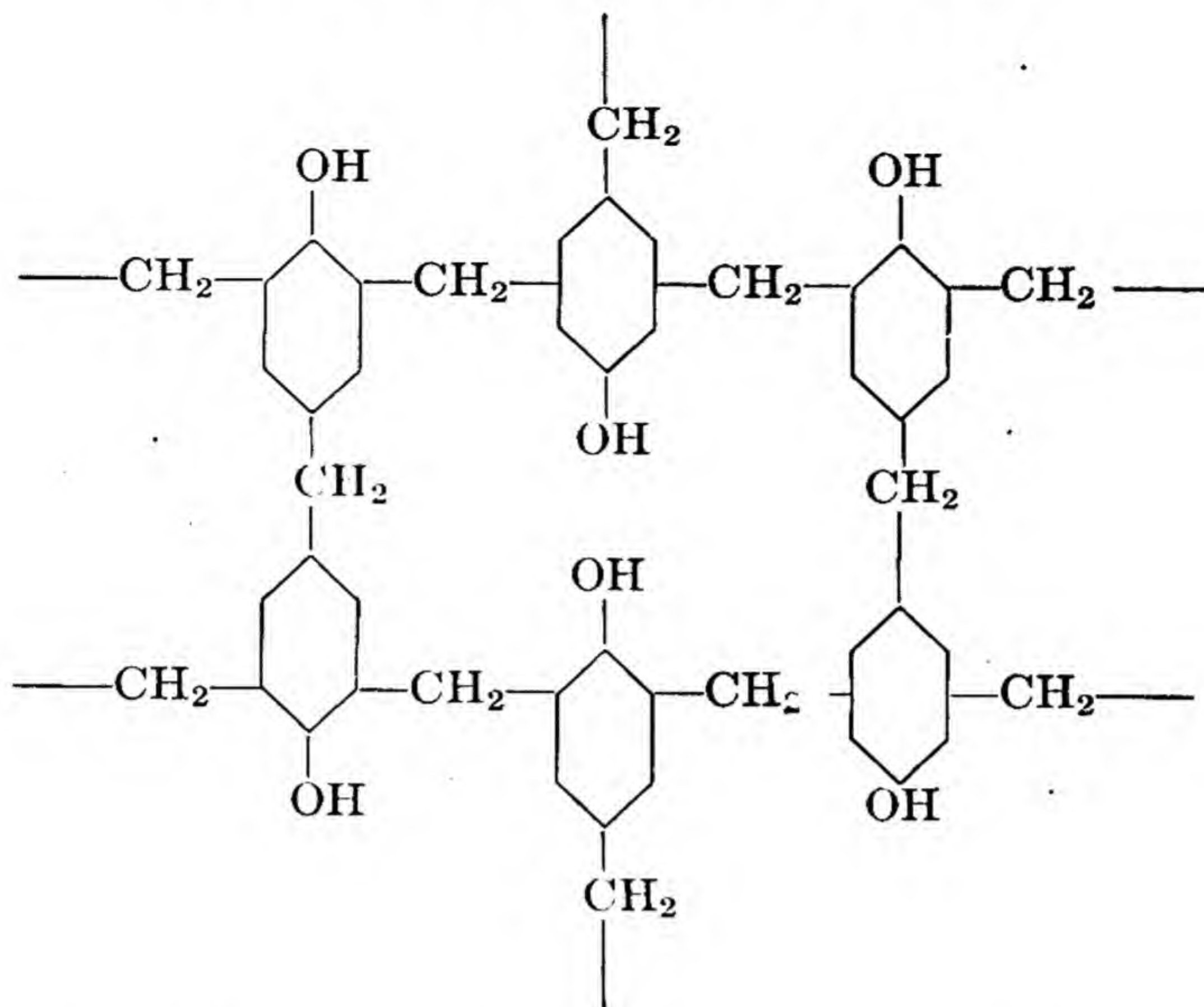
This structure is merely a simplified representation of a very complex three-dimensional structure. Ether linkages are also formed, and there is considerably more irregularity than is implied in the diagram.

These resins, when classified according to the nature of the reaction occurring during their production, are of two fundamental types.[1]

One-stage Resins.—In these, all the necessary reactants (phenol, formaldehyde, catalyst) required to produce a thermosetting resin are charged into the resin kettle in the proper proportions and react together. An alkaline catalyst is used. The resin, as discharged from the kettle, is thermosetting or heat reactive and requires only further heating to complete the reaction to an infusible, insoluble state.

Two-stage Resins.—Only part of the necessary formaldehyde is added in the kettle in making these resins, and an acid catalyst is used. They are permanently fusible or thermoplastic when discharged from the kettle, but will react with additional formaldehyde to produce a thermosetting resin.

This additional formaldehyde is furnished by "hexa" (hexamethylene tetramine), a white crystalline solid that is added during subsequent processing and breaks down under the influence of heat into formaldehyde and ammonia. The formaldehyde combines with the resin and converts it to a thermosetting product; the ammonia serves as a catalyst for this second stage of the reaction.

Both one- and two-stage resins are used, separately or in combination,

[1] DONAHUE, F. J., *Modern Plastics*, **22**, 130 (1945).

in commercial molding materials.   Both types are believed to polymerize to similar end products.

The properties of the finished product are due to formation of a compound built up of a relatively large number of original reaction products so linked together that a very complex three-dimensional structure results. The variation in properties of these finished products must depend, at least to a certain extent, on the course of the polymerization.

•The raw materials used in the manufacture of phenol-formaldehyde resins are phenol and phenol derivatives such as resorcinol or para-isobutyl phenol, cresols, formaldehyde, and hexamethylene tetramine. Formaldehyde is usually used as about a 40 per cent aqueous solution containing as much as 10 to 18 per cent methyl alcohol but only very small amounts of formic acid.   The solid paraformaldehyde may also be used.

Catalysts can be either acids or bases, depending on which type of reaction is desired.   Basic catalysts are usually sodium hydroxide, calcium hydroxide, ammonium hydroxide or, in some cases, hexamethylene tetramine, $(CH_2)_6N_4$.   Nearly any of the acids can be used.

The procedures used for both one- and two-stage resins are quite similar, and the same equipment is used for both types.   The principal differences between the two are in the phenol-formaldehyde ratio and the type of catalyst used.   For one-stage resins, the ratio is approximately 1:1 and an alkaline catalyst is used.   Acid catalysts are employed for two-stage resins, and the phenol-formaldehyde ratio is about 1.5:1.

The production of phenol-formaldehyde resins involves a reaction that must be controlled.   Phenol and formaldehyde are introduced to a steel or nickel reaction kettle together with the desired catalyst and brought up to temperature.   Since the reaction is exothermic, it is necessary to shut off the heating steam and introduce cooling water into the jacket as soon as the kettle and ingredients are brought up to temperature.   In addition, a reflux condenser is necessary to prevent loss of formaldehyde.   Once the reaction is under control, heating is continued until the contents of the kettle separate into two layers: the heavier viscous resin and an aqueous layer.   At this point, vacuum is applied and the water driven off.   The time of heating and dehydration as well as the temperature must be carefully controlled as the product of the reaction must be a resin in the A stage, soluble in organic solvents and still thermoplastic.

Careful tests of reactivity, softening point, viscosity, and solubility are made at intervals on samples taken from the kettle while the distillation proceeds, and when the proper end point is reached, the resin is dropped from the kettle onto steel cooling floors where it is allowed to cool as rapidly as possible (see Fig. 67).•

After solidification, the fused mass is broken up by hand and ground to a fine powder.   This base resin powder is mixed with fillers and any desired

coloring agents, first in ribbon mixers or ball mills and then on heated mixing rolls. The heat supplied by these rolls carries the reaction a little further along so that the finished molding powder is in the B stage—nearly
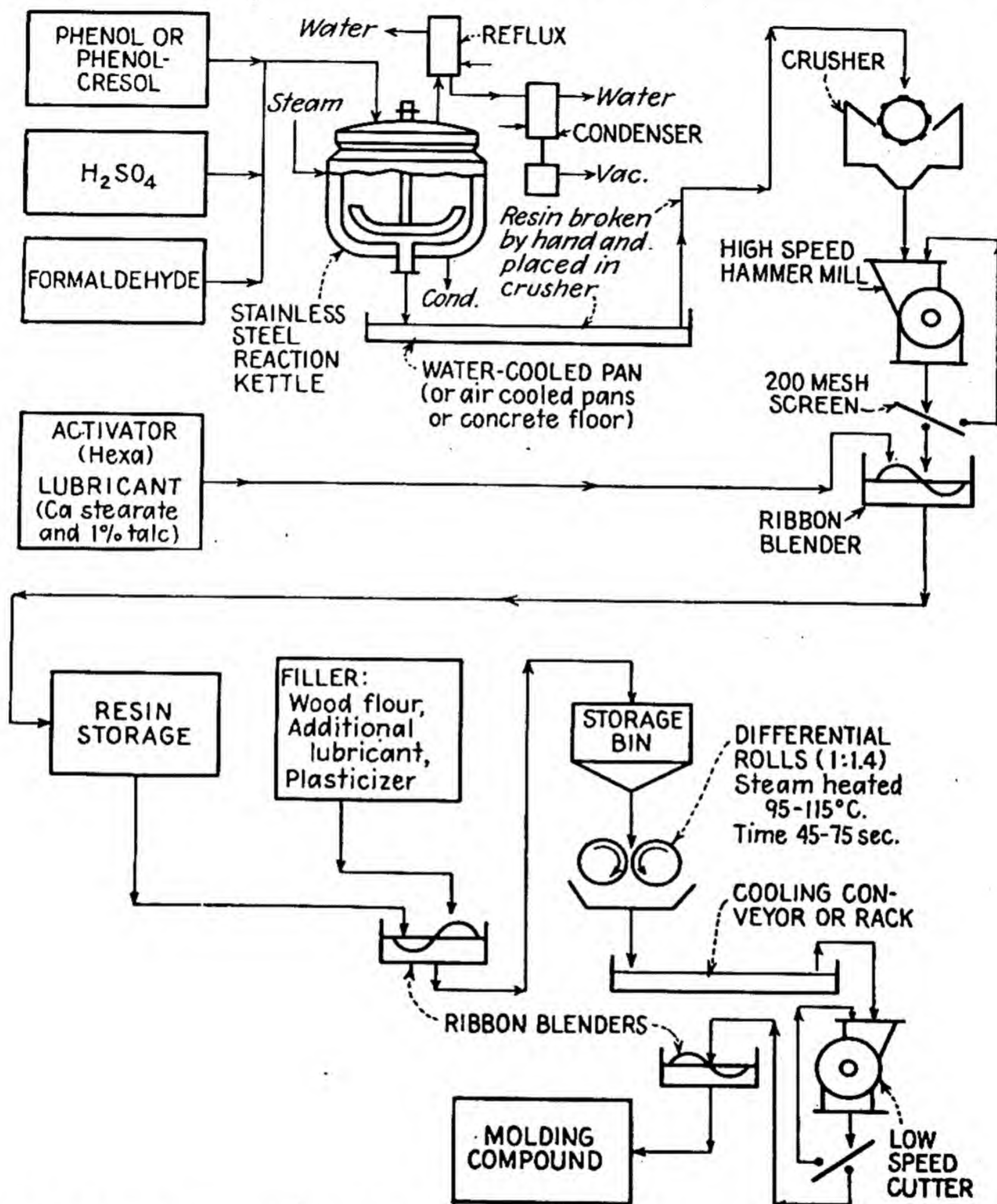
FIG. 67.—Flow sheet for phenol-formaldehyde molding powders. (*Chem. and Met.*)

insoluble in organic solvents but still fusible under the application of both heat and pressure. This stage, or the extent to which the reaction has been carried, is very important. The reaction must have proceeded far enough so that the final infusible C stage is readily and rapidly reached with reasonable mold temperatures and pressures; yet the molding com-

pound must still be fusible enough so that it will flow readily and fill all the mold cavity.

These resins are usually incorporated with fillers that not only reduce the cost, but often impart desirable qualities to the finished products (see Fig. 68). Pigments or dyes, a lubricant to make molding easier, and sometimes hardening agents are also added. The various materials are mixed thoroughly and then run between hot rolls to create a homogeneous mass and reduce the bulk. The material coming from the rolls is broken
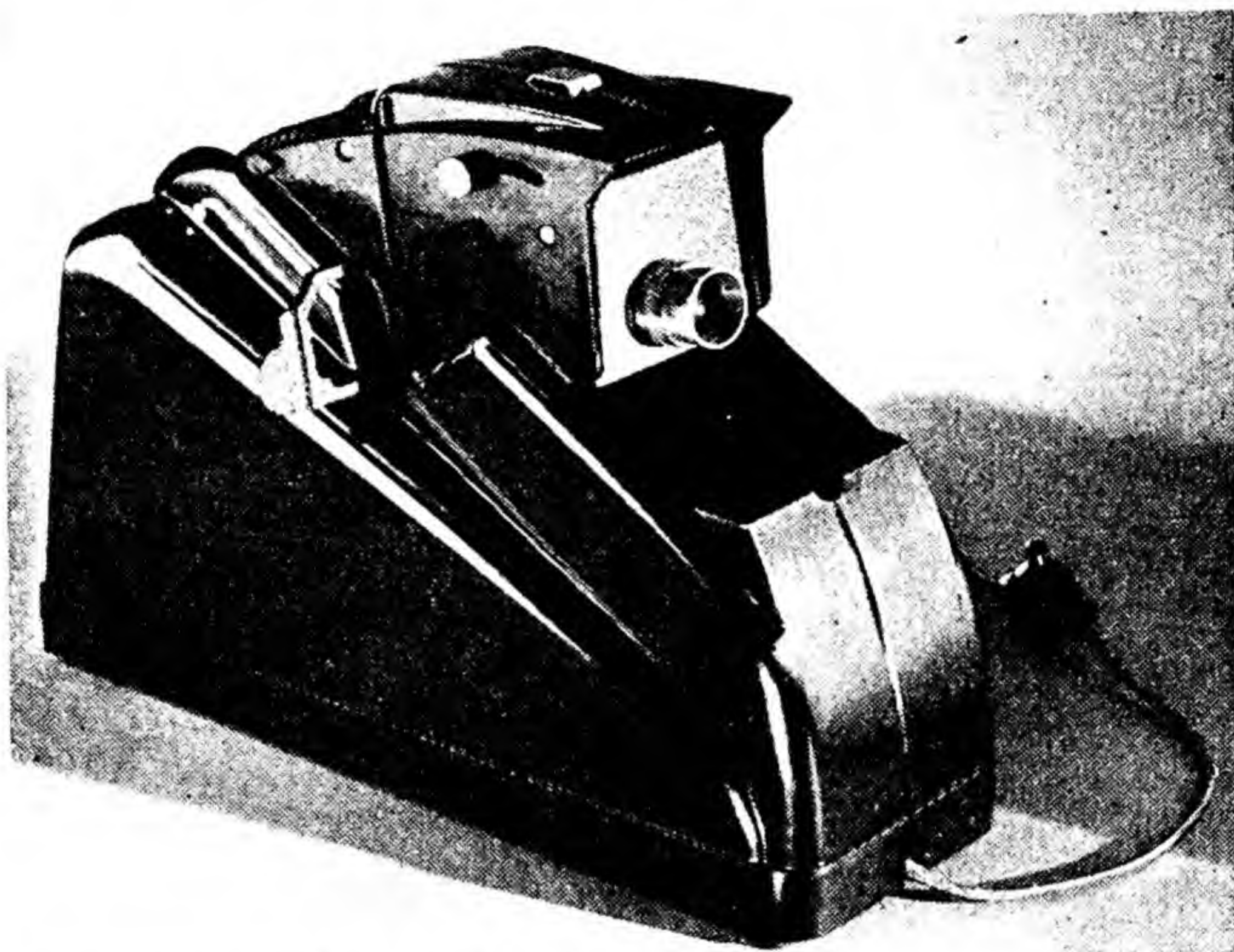
Fig. 68.—A microfilm projector molded from phenol-formaldehyde resin. (*Durez Plastics & Chemicals, Inc.*)

up, ground, and screened to the desired particle size. The resulting commercial molding powder is then packaged and shipped.

The principal fillers are

1. *Organic fillers*

   a. Wood Flour.—This is the cheapest and commonest filler. Softwoods such as white pine are usually used because of the light color and good resin-absorption characteristics. The flour is ordinarily ground to approximately 100 mesh and has a moisture content of less than 8 per cent. Wood flour has good molding properties and fair physical properties. Its moisture absorption is high, however, resulting in nonuniform electrical characteristics.

   b. Walnut-shell Flour.—Walnut-shell flour produces a very smooth surface with a medium gloss. Water absorption is lower than for cotton-cellulose fillers, but shrinkage is greater than for wood flour-filled material.

Strength and other physical properties are comparable to those of wood-flour-filled material, but the cost is higher.

c. Cotton Flock-chopped Canvas, Twisted Cord, and Cotton Flock.— These are textile by-products. Flock used in black and brown materials may be fairly dark in color, but bleached flock must be used for light-colored materials. This filler improves impact strength, and mold shrinkage is less than when wood flour is used, but bulk factor is higher and pourability poorer, making preforming more difficult. Water-absorption and electrical properties are about equal to wood-flour material.

d. Chopped Fabric.—This filler raises impact strength to a value twelve times above that of wood flour, but it has a bulk factor four times greater and cannot readily be preformed. Water absorption is higher, and electrical properties are poorer.

e. Twisted Cord.—Twisted cord imparts the highest impact strength to phenolic molding compounds, without sacrificing flow. Cord-filled material has a lower bulk factor than fabric-filled material but resembles it in water absorption, electrical, preforming, and molding properties.

2. *Inorganic Fillers.*—Inorganic fillers have some advantages over organic fillers but are not as widely used except for special-purpose molding powders. They have better dimensional stability, moisture absorption, heat resistance, and chemical resistance as compared with wood flour and other cellulose fillers. The principal inorganic fillers are as follows:

a. Asbestos.—Asbestos is used in the form of a finely ground powder in heat-resistant, chemical-resistant, and water-resistant formulations. It increases the heat resistance of the material and decreases water absorption and shrinkage, but it lowers flexural and tensile strength and raises the specific gravity, both of which are objectionable.

b. Diatomaceous Silica.—This filler improves the appearance, heat-resistance, and electrical properties of molded articles without increasing the specific gravity as much as an equivalent amount of asbestos. Its disadvantages are its abrasive character and tendency to wear molds and cause sticking. For this reason it is usually mixed with other less abrasive fillers.

c. Mica.—The advantages of this filler are its excellent electrical properties: high dielectric strength, low power factor, dielectric constant, and loss factor. Its low water absorption tends to maintain these good electrical properties in the molded parts in use. However, it has some undesirable characteristics. It is not wetted readily by the resin, and materials in which it is used may show poor coverage after molding, tending to cause a mottled appearance and induce sticking or poor release in the mold. Shrinkage of the molding material is less than with wood flour, but mechanical strength is also lowered, and specific gravity is increased.

A special application of inorganic fillers bonded with phenol-formalde-

hyde resins is in the manufacture of Haveg, a development used extensively in the construction of chemical equipment of corrosion-resistant properties. Both asbestos and graphite are used as fillers. Molding is done in inexpensive wooden molds under moderate heat and pressure. Tanks, piping, fittings, and pumps are obtainable for special applications
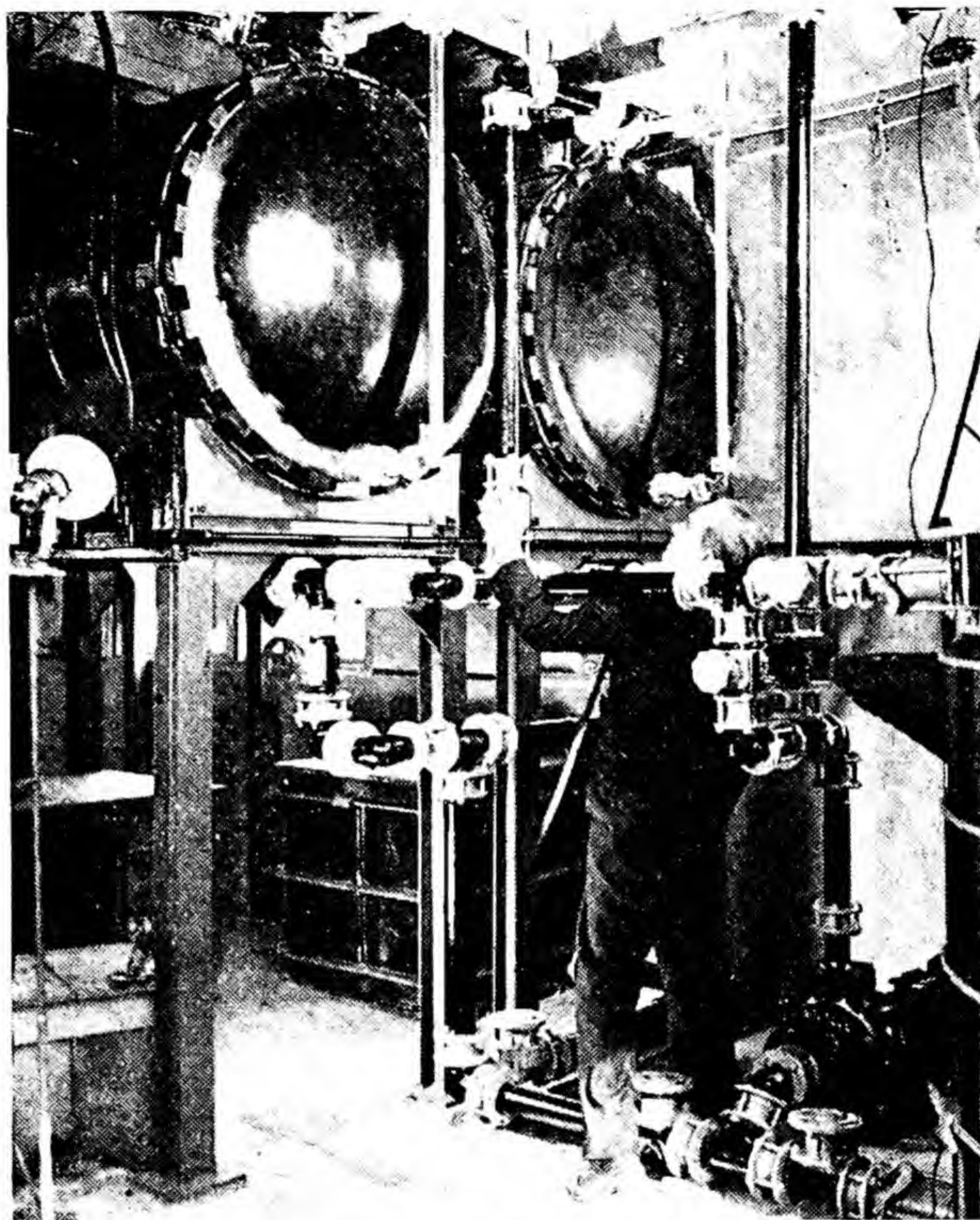
FIG. 69.—Tanks and piping of asbestos-filled phenol-formaldehyde molding composition. (*Haveg Corp.*)

(see Fig. 69). The asbestos-filled material is resistant to most acids and practically all salt solutions, and the graphite type is particularly useful in handling hydrofluoric acid up to temperatures of 130°C.

In addition to fillers, most molding compounds contain pigments or dyes to produce a smooth uniform color. The amount of colored pigment or dye used will vary between 2 and 4 per cent, depending on the tinting strength of the pigment, the color of the resin, and the color desired in the material. Carbon black or nigrosine is usually used to produce black molding powder, carbon black being preferred for applications where the material must not bleed in contact with alcohol or other solvents. Since carbon black is a semiconductor of electricity, materials containing it have

poor electrical properties. Nigrosine is used in general-purpose materials and electrical materials in which nonbleeding properties are not an essential requirement of the application.

Either organic dyes or inorganic pigments can be used to produce brown colors. Pigments are preferred because they can be more readily dispersed in the material without excessively long mixing.

Although a wide variety of medium and dark colors can be obtained, no light or pastel shades are possible since phenolics are inherently dark in
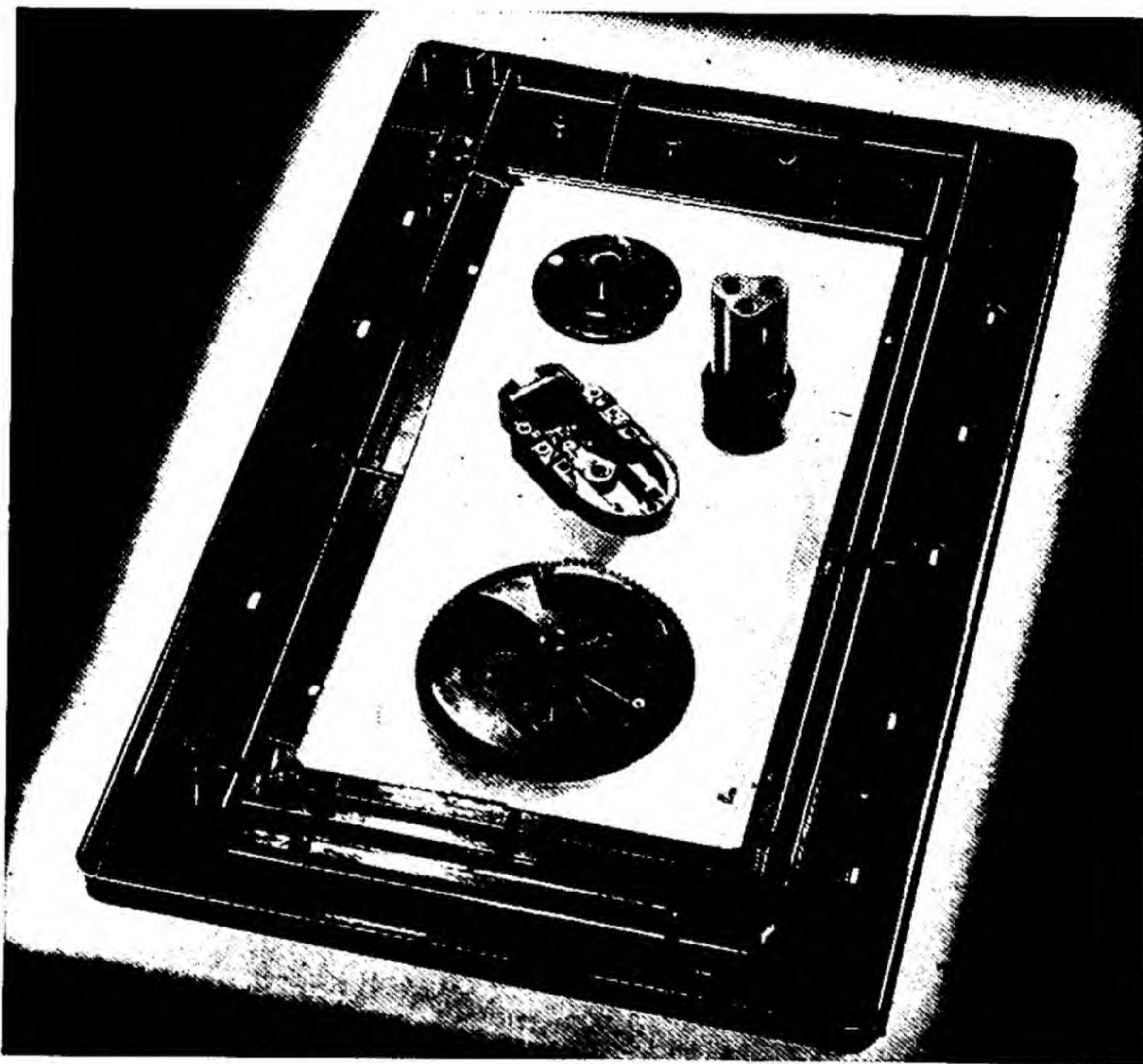
FIG. 70.—Complicated parts molded from phenol-formaldehyde molding powder.

color and darken further on exposure to light. Because of the dark color of the resin, it is necessary to add a certain amount of opaque white pigment along with the colored pigments or dyes for even the medium shades.

In spite of the dark color and lack of light fastness of phenolic resins, a large volume of phenolic materials is produced in medium bright shades of red, green, blue, orange, and light brown for closures, buttons, and novelties. Of these, the reds, oranges, yellow-greens, and browns are the most stable, since these colors approximate the colors of the base resin.

Mold lubricants form another class of additives that are ordinarily incorporated. Because of high molding pressures, the molded part is forced

against the mold surface with considerable pressure. Every minute detail and toolmark in the mold is reproduced on the molded piece (see Fig. 70). Since the contraction in volume of the piece in the mold resulting from polymerization is extremely slight, means must be provided for aiding the release of the piece from the mold. Various lubricants are ordinarily incorporated in the molding powder to facilitate the removal of the molded object. These lubricants are usually vegetable and mineral waxes, fatty acids, and metallic soaps.[1] Examples are

Mineral waxes......................Ceresin, paraffin
Vegetable waxes....................Carnauba, montan, candelilla wax
Fatty acids........................Stearic acid, oleic acid
Metallic soaps.....................Zinc stearate, calcium stearate

Carnauba and montan wax are the most efficient lubricants but are somewhat difficult to incorporate properly in the material.

None of these lubricants is truly compatible with the cured resins and will bloom or sweat out if used in amounts greater than approximately 3 per cent by weight of the base resin. The presence of excess lubricant tends also to lower the mechanical strength of the molded part.

Molding powders are supplied in the following grades:

General-purpose   Moisture-resistant
Impact-resistant   High-dielectric
Heat-resistant   Acid-resistant
Nonbleeding   Alkali-resistant
Arc-resistant

In addition, the rate at which the heat-plasticized resin will flow in the mold is carefully controlled to ensure proper filling of the mold cavities under normal molding conditions.

PROPERTIES AND USES

OF

PHENOLIC MOLDING COMPOUNDS

Advantages:
    Ability to withstand high temperatures (400°F.)
    Excellent aging properties
    Good moldability
    Good impact strength (with special fillers)
    Good flexural strength
    Good weathering properties
    Fair tensile strength
    Fair electrical insulating properties
    Nonflammable
    Low cost

[1] DONAHUE, F. J., *Modern Plastics*, **22**, 130 (1945).

Disadvantages:

> Poor tracking and arcing resistance
> High density
> Availability in dark colors only

Common uses:

> Airplane and automobile parts
> Cases for small cameras
> Control panels
> Radio cabinets
> Switch boxes
> Telephone equipment
> Electrical appliances
> Buttons, knobs, and ornaments
> Chemical equipment

Cast Phenolic Resins.—Variations in the condensation reaction between phenol and formaldehyde produce resins that have entirely different applications. These resins are unique in that they are cast directly from the reaction kettle, contain no filler, and the transition of the initial liquid to the final insoluble infusible product takes place over relatively long periods of time in open molds at atmospheric pressure and at temperatures considerably below 100°C. The products differ considerably from the molded phenolics, particularly in regard to color and appearance.

Phenol and formaldehyde in the proportion of 1 to 1.5 to 2.5 moles are allowed to react in large nickel kettles using an alkali catalyst, usually sodium or potassium hydroxide, or sodium carbonate. As the reaction starts, the original water-white mixture is changed to a deep amber color. The reaction is allowed to progress either under vacuum or at atmospheric conditions for the desired period of time. The amount of catalyst and the time of reaction are controlled so that the resin will not precipitate from its water solution even when cooled to 10°C. When the reaction has proceeded to the desired extent, the aqueous resin solution is promptly neutralized and acidified with lactic acid, phthalic anhydride, or both. There is an immediate change in appearance from dark amber to an extremely light straw-colored product. Vacuum is now applied or continued until the resin has a water content ranging from 5.0 to 10 per cent, depending upon the product desired. There is considerable flexibility in kettle operation without obtaining a water-insoluble resin. As the hot liquid resin comes from the kettle, it has the clarity, color, and flow of the lightest corn sirup. Presumably linear chains or low polymers have been produced, giving typical condensation products that are still wholly fusible and soluble. At this stage they are usually poured while still hot into molds and polymerized by heat to the final products, which are infusible and insoluble. Since these liquid resins are poured immediately into open molds, which may be up to 30 in. in length, it is important that the chemical reaction

in the kettle and the vacuum dehydration be adjusted to produce a resin of just sufficient viscosity and body to permit the occluded air bubbles to escape completely before polymerization and gelation begin.

The transition from the liquid phase of the resin to the infusible insoluble end product is accomplished by heating it at atmospheric pressure in open molds for 3 to 7 days at temperatures of 65 to 80°C. (see Fig. 71). As
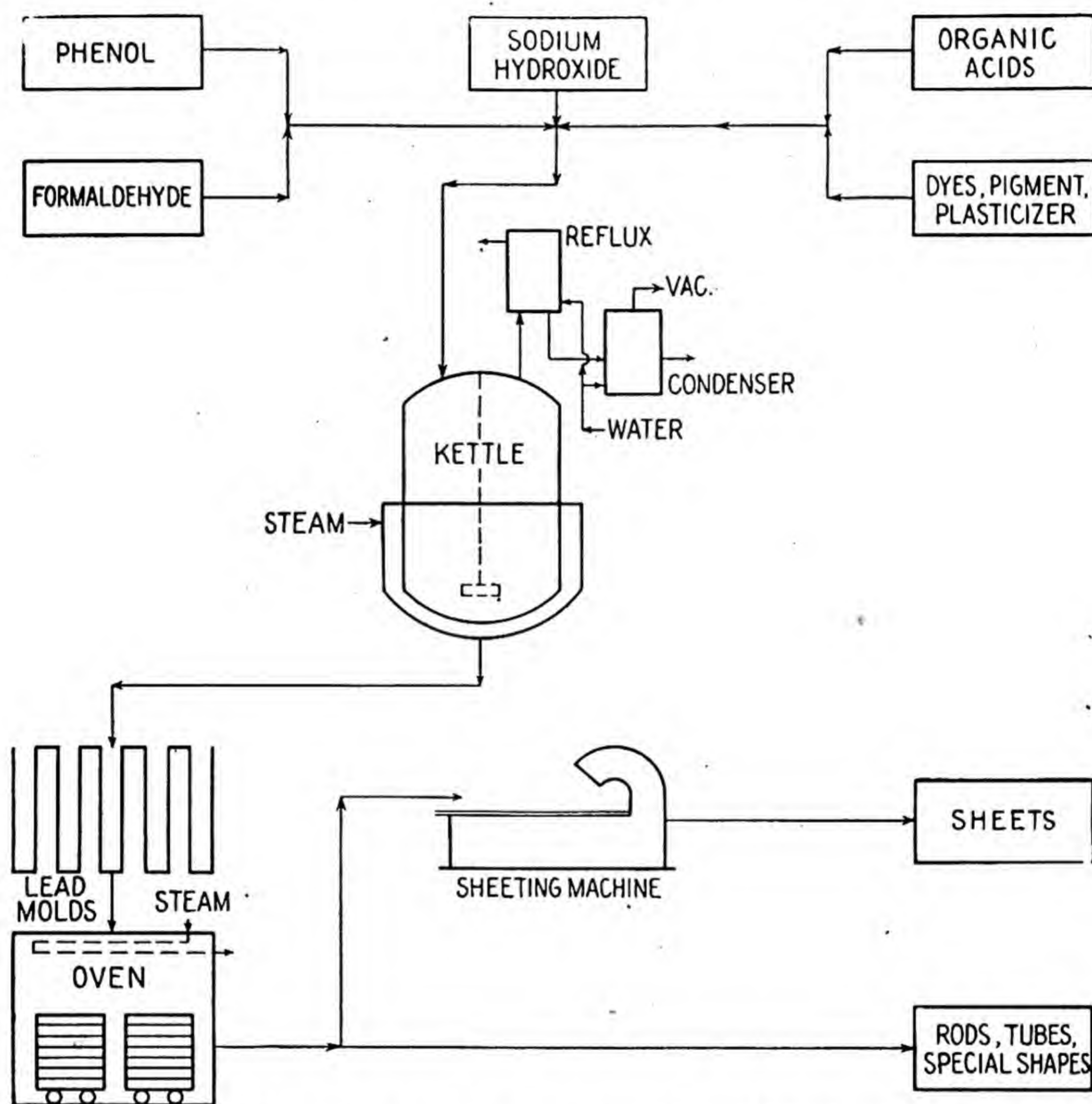
FIG. 71.—Flow sheet for cast phenol-formaldehyde resins.

heat is applied in the ovens, a gradual chemical conversion takes place transforming the resin first to a soft tacky gel, which gradually hardens to the final product without loss in weight. Definite physical changes take place during the reaction. During the first 10 to 16 hr. the resin gels slightly but maintains its clarity, indicating the extreme water tolerance of the system. If a sample is cooled at this stage, the water separates in finely dispersed droplets and the resin immediately becomes opaque. The heat-hardened end products still contain particles of water of colloidal size.

Actual measurements of these water droplets, with different water contents in the cured resin, indicated a variation in diameter from 6 to 8 microns to 0.2 micron.[1]

Water plays an important part during the formation of the liquid resin as well as during the sol-gel transformation to the hard end products. The size of the water droplets not only affects the physical properties of the resin, but it also contributes to its color and appearance. When the water content is high, the end product resembles translucent ivory. With progressive reduction in size of the water particle, a point is reached where the translucence disappears and the resin takes on a dense chalk-white appearance. If the water content is still lowered below this optimum point, the product again becomes translucent. These various effects can be obtained by careful control of the reaction conditions.

Cast phenolic resins have many unusual and desirable properties. Among thermosetting compounds they are unique in that they are cured at atmospheric pressure and are composed of 100 per cent resin without the incorporation of any filler. Their strength under tension, impact, and compression is comparable with that of many phenol-formaldehyde molding powders. The presence of finely divided water droplets not only produces an excellent appearance, but also acts in a manner comparable to fillers in improving the physical properties of the finished articles. In addition they are nonflammable and nonabsorbent, odorless, tasteless, and range in color from opacity through translucency to water-white transparency. A special grade may be produced by using barium hydroxide as the catalyst instead of caustic soda. Sulfuric acid is used for neutralization in place of an organic acid, dispersing very finely divided barium sulfate throughout the mass in addition to the dispersed water.

This casting method of fabricating is less expensive and less time consuming than compression molding, where the number of pieces is relatively small. In such a case, the cost of a hardened steel mold would be excessively high per unit.

Cast phenolics are available as standard polished or unpolished sheets, rods, and cylinders and can be obtained as special cast shapes (see Fig. 72) Special rods are available in such forms as square, octagon, and fluted.

In general, cast phenolics have high compressive, tensile, and flexural strengths in the absence of fibrous fillers. They also have good adhesive and electrical insulating properties, are easily machined, and have a high luster when polished.

[1] THOMPSON, W. R., Chem. Ind., 48, 45 (1941)
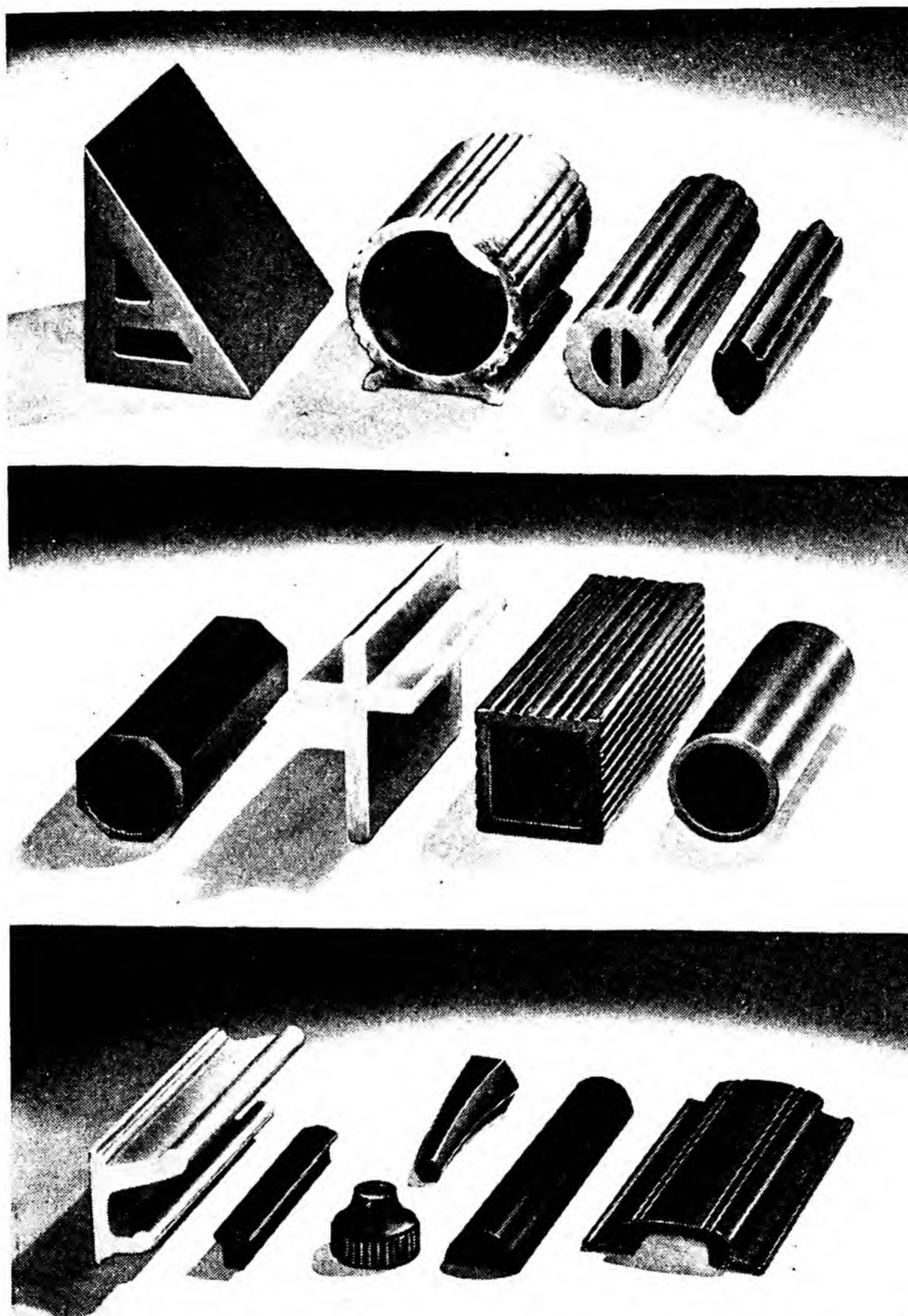
FIG. 72.—Special shapes of cast phenol-formaldehyde resin. (*Marblette Corp.*)

PROPERTIES AND USES
OF
CAST PHENOLIC PLASTIC

Advantages:

Machinability
Good tensile and impact strength
All colors; opaque or transparent
Nonflammability
Ability to withstand high temperatures
Excellent appearance

Disadvantages:

Restricted to cast articles
High density
High cost of small objects

Common uses:

Aircraft production tools
Industrial cabinet housings
Drawer pulls
Jewelry, novelties, games
Instrument dials
Interior lighting fixtures
Laminating varnishes for translucent panels
Colored flashlight lenses

Other Applications of Phenolic Resins.—By varying the conditions of the condensation reaction, catalysts, raw materials, ratios of raw materials and by the incorporation of other resins and addition agents, special products can be produced that have become important in the various applications of resins. Various varnish resins may be made that are widely used in different types of coatings, and a wide range of adhesives are produced. A recent development is the production of special "ion-exchange" resins for the purification or alteration of aqueous solutions. Two types of ion exchangers are available, cation exchangers and acid adsorbents. The cation adsorbents are supplied in a granular form similar to the zeolites and are capable of removing essentially all the metallic elements forming the cations in water solutions. They are easily regenerated with an acid. The acid adsorbents will remove the anions from water solutions and are regenerated with bases. A combination water-treating unit using the two types in series is capable of producing water of extremely high purity, containing only slightly more dissolved impurities than distilled water. This process is frequently called "demineralizing" and promises to become important in lowering the ash content of special sugars and other process solutions as well as in water treatment.

Phenolic resins for coatings have become extremely important. They are used for enamels and varnishes and supply a high percentage of the

total resins used for this purpose. They may be classified into thermosetting and permanently fusible types. The thermosetting products generally result from reactions made with alkaline catalysts and with an excess of formaldehyde over the equimolecular proportion, while permanently fusible resins are obtained by the use of acid catalysts and a lower formaldehyde ratio. Both of these classes may be subdivided again into oil-soluble and spirit-soluble resins.

The oil-soluble heat-hardening resins are widely used with natural resins such as rosin and ester gum. A marked improvement is obtained in drying rate, moisture resistance, and durability of the varnishes so produced. These resins are also incorporated directly into drying oils without modification, as well as in combination with other resins, to produce baking coatings useful as coatings for cans, drums, tanks, and other articles that can be baked.

The spirit-soluble or non-oil-soluble resins are dissolved in volatile solvents to give varnishes that are used to produce exceptionally hard coatings having excellent resistance to moisture, most solvents, and many corrosive chemicals. This type of resin requires heating for final hardening. They are the oldest form of phenolic resin varnishes and have been popular as baked finishes for food containers, drums, tanks, tank cars, brass fixtures, razor blades, chemical equipment, and many other uses where their unique hardness and impervious nature are required. They are, however, too brittle to withstand extreme flexing or rough mechanical treatment.

Spirit-soluble permanently fusible resins have had only limited application in the coating field. Attempts have been made to use them as shellac substitutes, but they were never entirely satisfactory for this purpose.

The oil-soluble permanently fusible resins are now the most widely used of all the phenolic resins for coatings. They are available in many different grades, both as unmodified 100 per cent phenolic resins and in combination with rosin or other natural resins. The unmodified resins are made oil-soluble by the use of substituted phenols, such as para-tertiary butyl phenol, para-tertiary amyl phenol, or para-phenyl phenol. These substituent groups not only are oil-soluble but they replace the active hydrogen atoms in the benzene rings that are normally involved in the formation of cross linkages and cause these resins to resemble thermoplastic rather than thermosetting materials.

The unmodified resins are used in a high percentage of the air-drying oleoresinous varnishes and enamels, particularly those intended to withstand severe moisture conditions, weak alkalies and acids, and exterior weathering. They are cooked with drying oils, such as tung, linseed, dehydrated castor, soya, or other oils in various proportions, depending on the particular varnish or enamel being produced. Spar varnishes, or coatings for exterior use on wood, contain two to three parts of drying oil

to one part of resin, whereas coatings designed for use on metal may contain a larger proportion of resin. The latter are used as anticorrosive primers for automobile bodies, structural steel, bridges, dams, ships, railway equipment, and numerous similar uses.

In the last few years, many special types of phenol-formaldehyde resins for use in coatings have been developed. One of these employs a reaction between phenols and various terpenes to give a hard, brittle resin capable of yielding quick-drying varnishes of accepted quality. Another type of phenolic resin coating employs the reaction product of a phenol with a drying oil. These varnishes have been used as coatings for cloth where good resistance to weathering is required.

A process has been developed that enables phenolic resins to be dispersed in an aqueous medium. These resins first gained attention because of their property of drying through the evaporation of water, their slight penetration into porous sufaces, and the fact that surfaces did not have to be dry before being coated. Films deposited in this manner are highly resistant to the passage of moisture and possess good exterior durability. They have been used as primer vehicles, especially in the protection of aluminum alloys or steel against the corrosive effects of the weather and of sea water.

Phenol-formaldehyde resins are used in a wide variety of adhesives The oldest type was a heat-hardenable cement such as that used to seal light bulbs and radio tubes to their bases, bristles in brushes, and as a general bonding material. Recently a wide variety of phenolic adhesives and modified phenolic types have been produced. In general, they may be classified much like the resins used in coatings, and many of their uses depend on their solubility and thermal properties. The most important application is in the formation of plywood and in the bonding of wooden sections.

Resorcinol-formaldehyde resins.—Resorcinol or meta-dihydroxybenzene, is used in place of phenol in phenol-aldehyde resins to produce a thermosetting resin that cures at low temperatures. Resorcinol resins are produced that will cure at room temperature under neutral conditions, and all these resins will cure in a temperature range extending only slightly above the temperature of boiling water. This characteristic has many advantages. Presses may be heated by hot water circulating at constant temperature, giving a more uniform heat distribution. In the manufacture of laminates, the low temperature of cure is useful with materials that would be affected by higher temperatures.

The physical properties of these resins are in the same range as the phenolics, but they have not replaced the phenolics in molding-powder applications to any extent because of their much higher price. They also are considerably darker in color, which precludes their use for other than blacks and the very dark shades of red and brown.

Resorcinol-formaldehyde resin adhesives have been developed that will cure at approximately room temperatures with the addition of the proper hardening agent. This type of adhesive has an indefinitely long shelf life because it has no tendency to harden unless the hardener is added. The reaction then progresses quite rapidly so that within 4 or 5 hr. at 75 to 80°F. the mixed adhesive has reached its permanent set. By proper adjustment of the reaction mixture, practically any desired curing temperature may be obtained.

These adhesives were originally developed for the bonding of wooden members at room temperatures where higher temperatures could not be obtained, but they have been employed in bag molding and in the manufacture of laminated timbers and other types of wooden articles where higher temperatures are employed. Good results are also obtained in bonding other materials such as plastics, glass, and ceramic ware. In the field of metal bonding, and particularly the bonding of metal to other materials, these adhesives produce excellent bonds if the metal surface is first given a special priming coat.

A special latex has been developed that is based on a dispersion of these resins and has proved to be very effective as an adhesive for bonding rubber to cotton and rayon cords in the production of cord fabric for tires. At the present time, this is the largest single use for these resins.

Phenol-Furfural Resins.—The structural formula of furfural is as follows:

$$\begin{array}{c} HC\text{---}CH \\ \| \quad\quad \| \\ HC \diagdown \quad \diagup C\text{--}C{=}O \\ O \quad\quad\quad \diagdown H \end{array}$$
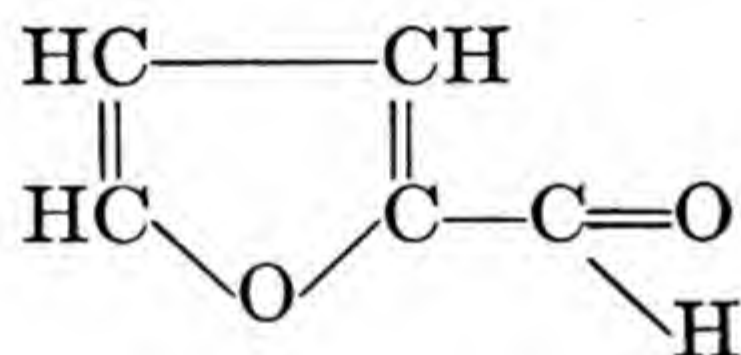
The furane ring structure contains two double bonds, and the aldehyde group is attached to the ring so that the conjugation of these double bonds is continued through the aldehyde group, making it particularly reactive. In the reaction with phenols, the aldehyde group reacts just as it did when formaldehyde was used. After the furfural has reacted with the phenol to form the initial reaction product, the furane ring with its conjugated system of double bonds also enters into the reaction, providing a network of thoroughly interlaced cross-linked molecular chains capable of complete cure, high strength, and exceptional impact resistance. The furane ring in combination with the aromatic ring structure of phenol produces a rather flat plasticity curve, resulting in unusual flow characterisitics, which has made transfer molding of these resins relatively easy. The flat plasticity curve gives good flow characteristics even under difficult molding conditions which makes these resins useful for the molding of long flow or large parts.

The furfural-phenol resins do not form the characteristic *A, B,* and *C* stages as do the phenol-formaldehyde resins, so that the partly cured non-flowing *B* stage is avoided, and the resins maintain their flow characteristics at temperatures just slightly above those required to induce plasticity over relatively long periods of time. But temperatures of 350 to 375°F. cause a very rapid exothermic cure to take place. Thus these resins can be made into molding compositions that flow readily either in transfer or compression molding until the mold cavity is filled and then cure rapidly as they come up to curing temperatures. The avoidance of the *B* stage and the ready cross polymerization at molding temperatures result in accuracy of dimensions and insert positions and a rigid cured part of high accuracy both as to dimensions and surface.

Furfural-phenol molding compounds are brown or black in color, though solid dark colors such as red, green, and yellow are obtainable. This dark coloration would be expected because of the furfural structure. They produce homogeneous moldings that eject from the molds clean, bright, and shining. Accuracy of dimension is good and is combined with high speed of molding.

Furfural resins were among the first in use for transfer molding. In many cases they are used in combination with other phenolics. In the phenol-formaldehyde combination, they are well adapted to this method, which provides high production and yields dark-colored products of good strength and infusibility.

Furfural resins are used as a quick-curing cement for bonding similar to those produced with phenol-formaldehyde. These cements must cure quickly, adhere to both metal and glass, and resist moisture and heat. Other adhesives for plywood and general use are produced. This resin is also used as the bonding agent for abrasive wheels.

UREA-FORMALDEHYDE RESINS

The development of these resins occurred along with the cheap production of synthetic urea and formaldehyde. Urea is made synthetically from carbon dioxide and ammonia, while formaldehyde is produced from methyl alcohol, which in turn is made from carbon monoxide and hydrogen. As the cost of urea and formaldehyde decreased with synthetic mass production, the importance of this type of resins increased. Although the reaction was first studied as early as 1884, it was not until nearly 1930 that these resins became of commercial importance.

Urea and formaldehyde condense to give a thermosetting resin. The chemistry of the reaction is not completely understood, but the reaction and structure is usually represented as follows:

$$\underset{\text{NH}_2}{\overset{\text{NH}_2}{\diagdown}}\!\!\!C\!\!=\!\!O + CH_2O \longrightarrow \underset{\text{NHCH}_2\text{OH}}{\overset{\text{NH}_2}{\diagdown}}\!\!\!C\!\!=\!\!O$$
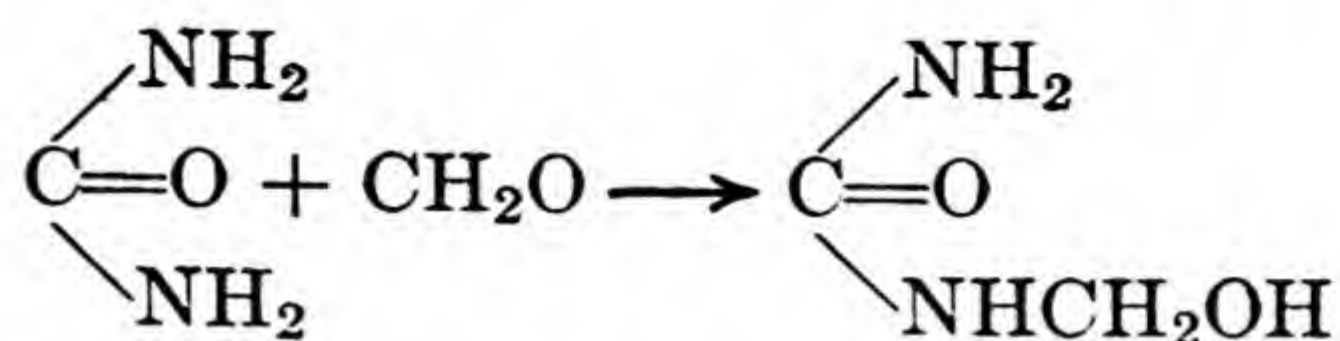
The monomethylol urea can react with another mole of formaldehyde to produce dimethylol urea, but under reaction conditions, condensation of the monomethylol urea will take place before all the NH_2 groups have reacted. A highly idealized reaction product of this condensation would result in a straight-chain polymer:

$$
\begin{array}{ccccc}
NH_2 & & NH_2 & & NH_2 \\
| & & | & & | \\
O\!=\!C & & O\!=\!C & & O\!=\!C \\
| & & | & & | \\
\!\!-\!\!N\!-\!CH_2\!-\!N\!-\!CH_2\!-\!N\!-\!CH_2\!\!-\!\!
\end{array}
$$
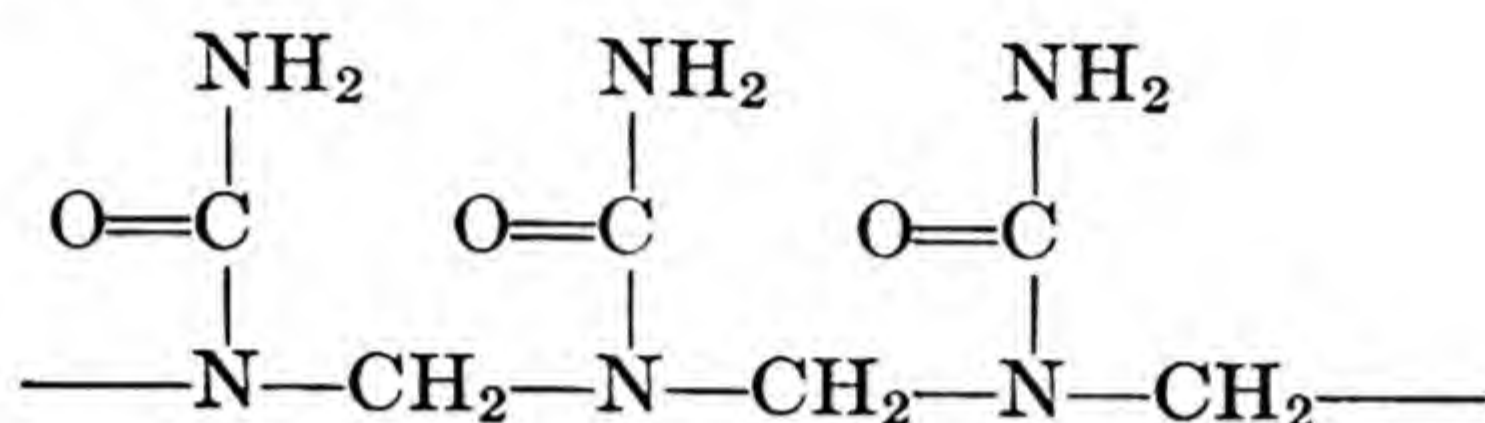
The free NH_2 groups indicated by this structure would, of course, have reacted to a certain extent. In any event, they are capable of reacting to provide a highly complex three-dimensional structure.

A variation of the preliminary condensation reaction involves the use of an alcohol to produce an alkyl-substituted monomethylol urea. Butyl or amyl alcohols may be used. The presence of the alkyl group greatly increases the oil solubility of the resin so that this modification is used for coatings.

In the unfilled form, these resins are clear, transparent solids resembling glass. When they were first discovered, there was a great furor—it was thought that an unbreakable substitute for glass had been found, but they are comparatively soft and too easily scratched. In addition, the polymerization reaction apparently continues extremely slowly even after molding. This reaction causes strains that result in surface cracks or crazing that spoils the surface polish of the clear resin. They are not completely water-resistant so that continued exposure to moisture also dulls the surface. The use of proper fillers moderates both of these troubles.

The urea and formaldehyde are condensed in kettles similar to those used for phenol-formaldehyde resins. The condensation takes place at slightly lower temperatures. The desired *A* product is soluble in water so that no separation into layers takes place. After partial dehydration, the aqueous solution of the *A* polymer is used to impregnate the desired filler. The filler is usually cellulose, either wood flour or sulfite pulp. A high percentage of filler is used to prevent surface cracking. The impregnation is done in a vacuum mixing machine and the resulting mixture dried to remove the water and carry the reaction to the proper stage. After drying, the resin is ground to the desired fineness in ball mills (see Fig. 73).

The importance of the urea-formaldehyde resins depends partly on the fact that the resin is water-white and clear. Thus light-colored or pastel shades can be produced. However, the water-white color of this resin is
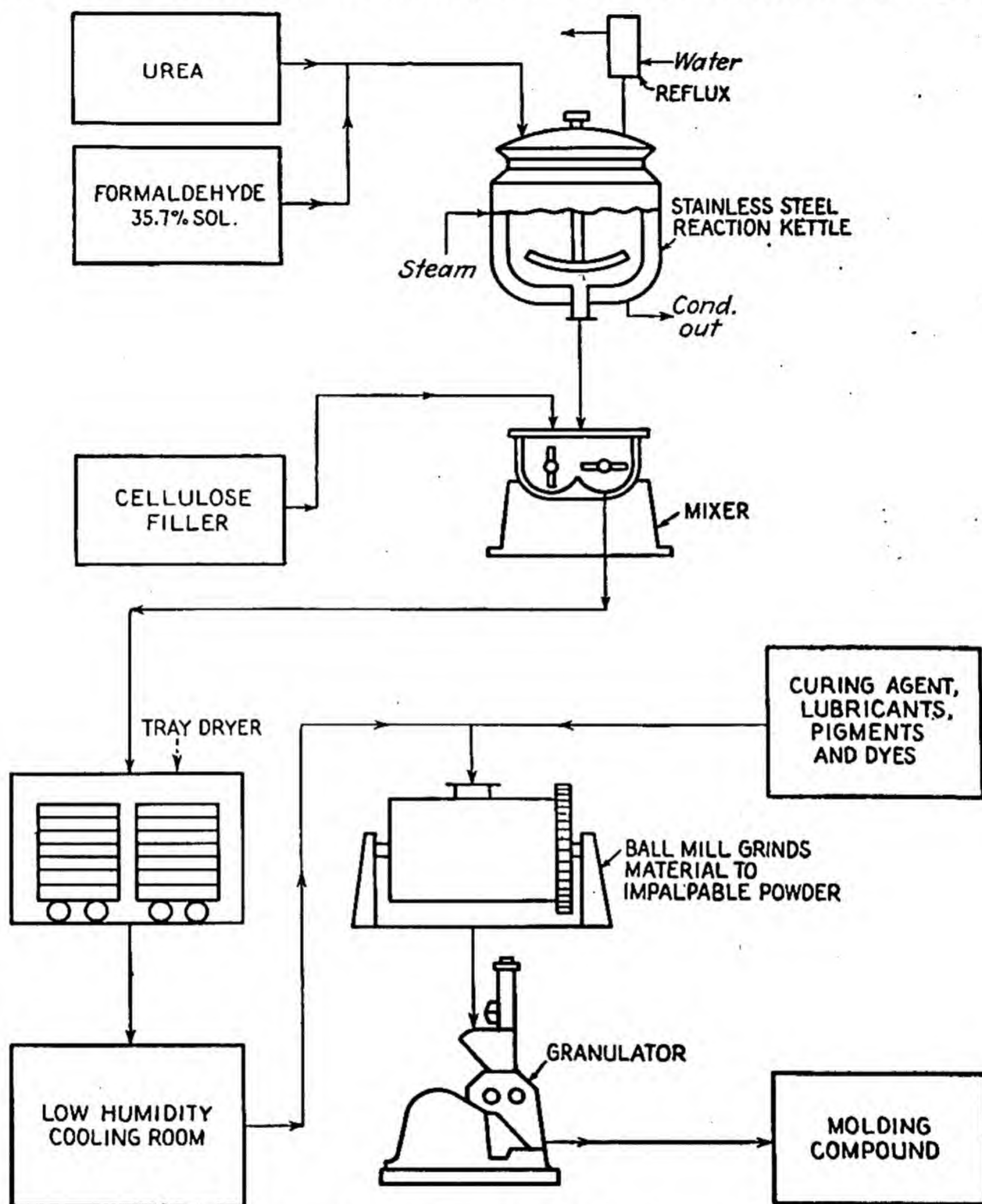
Fig. 73.—Flow sheet for urea-formaldehyde resins. (*Chem. and Met.*)

not its only advantage, since its tensile strength and hardness are better than the phenolics. The water resistance and impact strength, on the other hand, are considerably lower. The resin in the final cured state is thermosetting and resembles the phenolics in heat resistance, although it is inferior in this respect.

Since the intermediate *A* resins are water soluble, they find considerable

use in the production of adhesives, coatings, paper conditioners, and other products in which intermediate water solubility, followed by a complete cure by means of heat or catalysts, is a distinct advantage.

Urea-formaldehyde thermosetting molding powders are supplied in a partly polymerized state so that final curing under pressure takes place in the hot mold. The molded product is insoluble, infusible, tasteless, odorless, hard, and tough. It has good light-diffusing qualities, and its electrical properties, including nontracking characteristics, are good. It is completely resistant to oils, greases, and organic solvents but is attacked by concentrated acids and alkalies.

Urea resins are used to produce a wide variety of molded articles, such as buttons and buckles, knobs and handles, boxes and containers, bottle closures, instrument housings, tumblers and tableware, wiring devices, and molded shades and reflectors. In lighting equipment, translucent urea-formaldehyde is used for indirect lighting.

The resins that have been modified by the introduction of an alkyl group are used for the production of coatings by mixing them with alkyds, processed oils, and plasticizers. These resins are usually supplied in 50 per cent solutions in mixtures of naphthas and alcohols.

Coatings are usually baked at temperatures ranging from 225 to 325°F., although special catalyzed resins may be made to conform with low-temperature force-dry schedules. The urea resin content of such coatings hardens by polymerization as contrasted to evaporation and/or oxidation of the usual alkyd, oil, or lacquer film.

Urea-formaldehyde coatings are resistant to breakdown and discoloration when subjected to sunlight and exterior exposure. When formulated with coconut- and castor-oil alkyds, their clarity and color-retention properties produce high-quality coatings for refrigerators, kitchenware, bathroom and hospital equipment, etc. In combination with alkyds, they have shown outstanding interior and exterior durability.

The ureas are used to produce both the so-called "cold-setting" adhesives and the various grades of powders and water solutions requiring heat for final bonding. The excellent storage life and simple application methods have made these adhesives extremely important. In addition, they are exceeded in durability and strength only by the phenolics. The cold-setting type has a catalyst incorporated in the powder which does not become active until water is added. The use of catalysts makes it possible to use this adhesive at temperatures of 75°F., but it should not be used for much lower temperatures as the final cure is too slow. This type of glue has become a household article.

Water-soluble ureas mixed with starch are important adhesives in the field of packaging and labeling. They are far superior to starch or casein both in strength and water resistance.

The use of urea resins to impregnate wood promises to supply a new

material of construction. The wood is first impregnated with methylol urea, and then the polymerization reaction is carried out in the thoroughly impregnated material. This produces a denser, inert product that can be machined much the same as wood yet is much stronger and will not swell, shrink, or warp.

Doors, windows, and drawers can be constructed to close dimensions and not stick or become loose with changes in atmospheric conditions. Since the treatment imparts dimensional stability and allows smoother, cleaner, and more accurate machining, it is possible that items manufactured from wood could be assembled from finished standarized parts.

The wood that is to be treated should, for most purposes, be dry or at least dried below its fiber-saturation point. When the methylol urea solution is forced into the wood, it first enters the cell cavities. Then it rapidly diffuses into the cell walls where, under the influence of the acids of the wood, it promptly begins to polymerize.

For most veneers, up to 0.0625 in., it is not usually necessary to apply pressure above atmospheric to obtain adequate absorption. For deep penetration of lumber, pressure of 50 to 100 lb. or more per square inch are required. For sapwood of both softwoods and hardwoods and the heartwoods of some hardwoods, an impregnation cycle of 20 to 50 min. vacuum (26 to 28 in.) followed by 100 lb. per sq. in. pressure applied for 10 to 50 min. at room temperatures is usually sufficient.

A water solution of an uncondensed methylol urea is employed. This may be obtained by reacting urea and formaldehyde in the proper proportions and under controlled conditions. However, a simpler method is merely to dissolve urea and dimethylol urea (DMU) in water. For most purposes, 1 to 2 parts of urea and 6 parts of dimethylol urea dissolved in 20 to 24 parts of water are satisfactory.

If the wood is to be colored, water-soluble dyestuffs, neutral or slightly alkaline in solution, are added to the treating solution. The color produced is apparently not affected by the methylol urea.

<div align="center">

PROPERTIES AND USES

OF

UREA RESINS

</div>

Advantages:

> Nontracking characteristic
> Good electrical insulating properties
> Ability to withstand high temperatures (180 to 250°F.)
> Good moldability
> Resistance to organic solvents
> Availability in all colors

Disadvantages:

> Low impact strength
> Hardening and slight warping with age

Inability to withstand acids and alkalies

Relatively poor water resistance

Common uses:

Adhesives

Baking enamels

Buttons

Display packages

Light fixtures

Machine parts (laminated with canvas or wood)

Radio cabinets

MELAMINE-FORMALDEHYDE RESINS

Melamine resins and compounds were first produced commercially in the United States in 1939. Melamine is a trimer of cyanamide formed through the intermediate production of dicyanamide, as follows:

$$2H_2NCN \longrightarrow HN{=}C \overset{\displaystyle NH_2}{\underset{\displaystyle NH}{|}} \quad \overset{H_2NCN}{\longrightarrow}$$
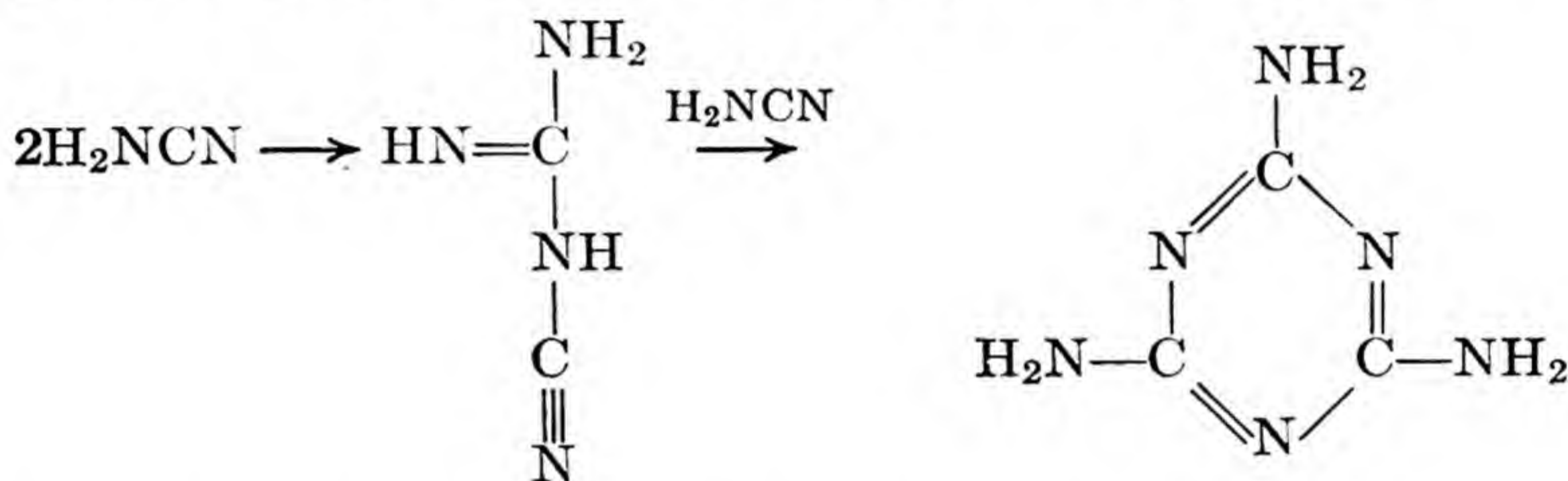
Melamine resins are produced by condensing melamine with formaldehyde in the same manner as in the production of urea-formaldehyde resins. Methylol derivatives are first formed, and the complex three-dimensional structure is built up by condensation.

The cellulose-filled molding powder is similar to the ureas in many respects. Molded articles, however, can be produced that are harder, have better heat resistance, and are less affected by water. A much wider range of fillers can be used than with the ureas. Special fillers such as asbestos can be used to produce exceptional heat resistance. The arc resistance is similar to the ureas, but the wider choice of molding conditions and fillers makes it possible to utilize this property to a greater extent.

Because of their greater inertness, hardness, and resistance to heat, melamine resins have been used for the production of translucent laminates and opaque laminates. In the production of opaque laminates, melamine is used on the surface lamina. Surface plies are frequently made with melamine resin to increase the arc resistance of the sheet. Melamine resin adhesives are being produced for exterior-grade plywood and for other special applications requiring improved quality and durability.

The molding compounds are handled and molded much the same as the phenolic compounds. Their molding cycle may be slightly longer due to

a longer period of flow. This flow gives excellent results in the transfer-molding process.

A recent application of considerable interest is their use for treating fabrics to prevent shrinkage. A monomer is applied in liquid form, and polymerization takes place in the fibers. As little as 2 per cent can reduce shrinkage by as much as 75 per cent and yet not change the softness or surface finish or appreciably affect the moisture resistance. This application promises to be extremely important in the production of high-quality woolens and cottons.

<div align="center">

PROPERTIES AND USES

OF

MELAMINE RESINS

</div>

Advantages:

   Ability to withstand high temperatures (500°F.)
   Ability to wet fiber-glass
   High impact strength with fiber-glass filler
   High abrasion resistance
   Good resistance to organic solvents
   Good arcing and tracking resistance

Disadvantages:

   High moisture absorption
   High power factor
   High cost

Common uses:

   Electric insulation (particularly at elevated temperatures)
   Laminating material for wood
   Molded tableware
   Outdoor signs
   Paper and glass fiber lamina
   Stove parts
   Coatings
   Treating paper and textiles

ANILINE-FORMALDEHYDE RESINS

The general reaction between formaldehyde and amines causes the formation of methylolamines:

$$RNH_2 + CH_2O \longrightarrow RNHCH_2OH$$
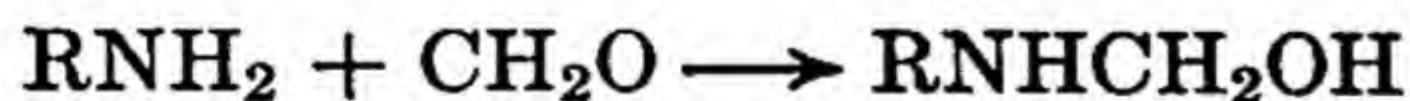
These compounds are usually unstable and lose water to form higher polymers derived from methyleneamines.

$$nRNHCH_2OH \longrightarrow (RN{=}CH_2)_n + H_2O$$
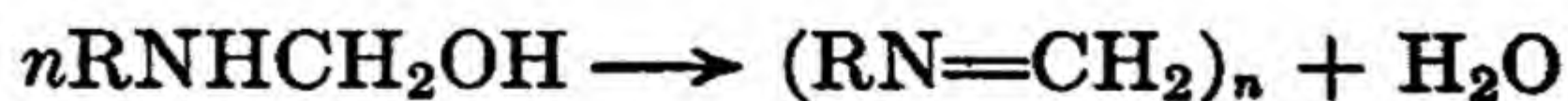
The condensation of aniline and formaldehyde produces an anhydro-formaldehyde-aniline resin $(C_6H_5N{=}CH_2)_3$ which is a six-membered ring.

$$
\begin{array}{c}
C_6H_5 \\
| \\
N \\
\diagup \quad \diagdown \\
CH_2 \qquad CH_2 \\
| \qquad\qquad | \\
C_6H_5 \longrightarrow N \qquad\quad N \longrightarrow C_6H_5 \\
\diagdown \qquad \diagup \\
CH_2
\end{array}
$$
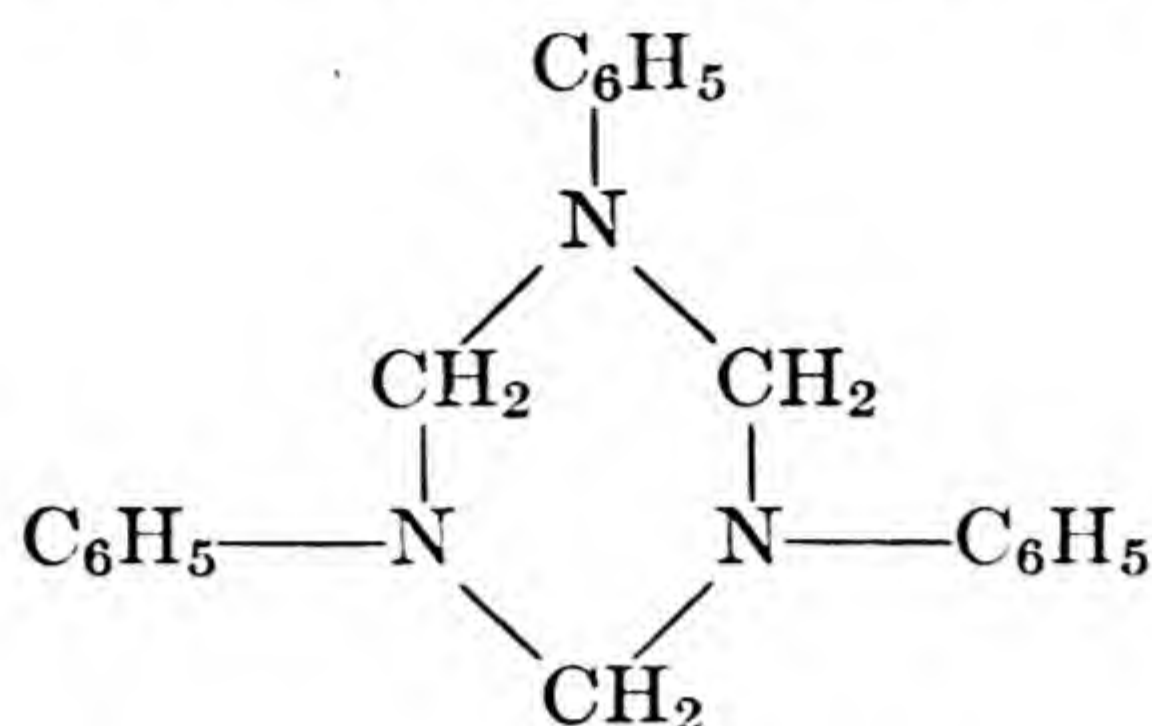
Some deviation from this formula is caused by the formation of higher polymers.

When one mole of formaldehyde is condensed with one mole of aniline in an acid solution, the resulting resin is fusible and soluble. As the molecular proportion of formaldehyde is increased, the resins become more and more insoluble and infusible. Thus a condensation product can be produced which is practically insoluble and can be molded readily in common molding equipment, but high temperatures are required. The pure resin is thermoplastic but does not possess the degree of plasticity necessary for injection molding. Fillers are not ordinarily used.

The molding technique required resembles that used for shellac. A temperature of 150 to 160°C. will soften the resin sufficiently to produce satisfactory results under pressures of 3,000 to 6,000 lb. per sq. in. The time element depends upon the softening rate and therefore is governed to a large extent by the thickness of the article being molded. After the article has been shaped, the resin is hardened by cooling the mold or press.

The pure resin is translucent and of a reddish-brown color. Electrical properties are good. The power-loss factor is very small and comparatively constant over a wide range of frequencies and atmospheric conditions. Moisture or oil absorption is negligible. It is not resistant to strong acids, is unaffected by alkalies, and is not soluble in any of the common organic solvents, including aromatics and alcohols.

Its low-loss properties and good electrical stability under the influence of moisture at ultra-high as well as at commercial frequencies make it suitable for applications in the radio field and in the expanding television industry. Such applications as coil forms, jack pile-ups, antenna housings, and tube bases are important. Terminal boards, strips, and blocks are other applications for which the material is especially suitable, in these cases because of its low conductivity in the presence of moisture.

POLYESTERS

The polyesters are formed by condensation reactions between polybasic acids and polyhydric alcohols. In order to form high molecular-weight polymers, it is necessary that the acid have at least two carboxyl groups

and that there be at least two hydroxyl groups in the alcohol molecule. If this is the case, condensation will produce long chain molecules, as follows:

$$HOOCRCOOH + HOR'OH \longrightarrow ---OOCRCOOR'OOCRCOOR'---$$

If either the acid or the alcohol contains additional hydroxyl, carboxyl, or many other reactive groups, it is possible to produce a three-dimensional thermosetting structure or to modify the resulting resin by adding on modifying groups.

The formation of polyesters received considerable attention from various workers in organic chemistry very early in its development. Berzelius reported some early work involving polyesters, and Smith took out patents on these compounds as early as 1901. Their commercial development was held up, partly due to the fact that their useful properties were not recognized, but mostly because of the high cost of polybasic acids. In the early part of this century, oxalic acid was the only dibasic acid available at low cost on a commercial scale, and this acid did not form a satisfactory resin. Then the dyestuff industry developed an inexpensive method for the manufacture of phthalic anhydride by the catalytic oxidation of naphthalene, using vanadium pentoxide as a catalyst. This acid—or rather its equivalent, the anhydride—is the most important acid in this field. Coupled with glycerine it forms the typical alkyd resin and is the base for a large variety of extremely important resins now being used for coatings.

These resins are the most versatile of all the coating resins because of the large variety of raw materials and modifying agents that may be used in their preparation. Most of the various acids and alcohols that might be used are given in the following list:

ACIDS

Phthalic	Pimelic
Malic	Suberic
Tartaric	Azelaic
Maleic	Sebacic
Citric	Camphoric
Succinic	Addition products formed from maleic acid
Glutaric	and vinyl acetate, styrene, rosin and other
Adipic	terpenes, and cyclopentadiene

ALCOHOLS

Glycerine	Mannitol
Ethylene glycol	Pentaerythritol
Propylene glycol	Diethylene glycol
Sorbitol	Polyethylene glycol

The various possible combinations from this list are almost unlimited even if the possibility of modification of these esters with other materials

were not present. Not all the acids and alcohols listed are commercially important at present, but they have been used at least in experimental quantities, and some of them would be used more generally if the cost of preparation were not quite so high.

The term "alkyd" is in general use in the coating field to designate a polyester type resin.

Since these polymers are used almost exclusively as resins for the preparation of varnishes, paints, and other coatings, their compatibility with oils and other resins is an extremely important factor. The straight polyesters, such as glyceryl phthalate itself, are not satisfactory in this respect and are modified by introducing another radical on the secondary carbon atom of glycerine. The modifying agent is usually a fatty acid or its equivalent and may be added to the glycerine molecule either before or during the condensation reaction. The net effect is to produce a polymer of the following type:

$$-\left[OOCC_6H_4COOCH_2CHCH_2 \atop \qquad\qquad\qquad |\atop\qquad\qquad\qquad R \right]_n-$$
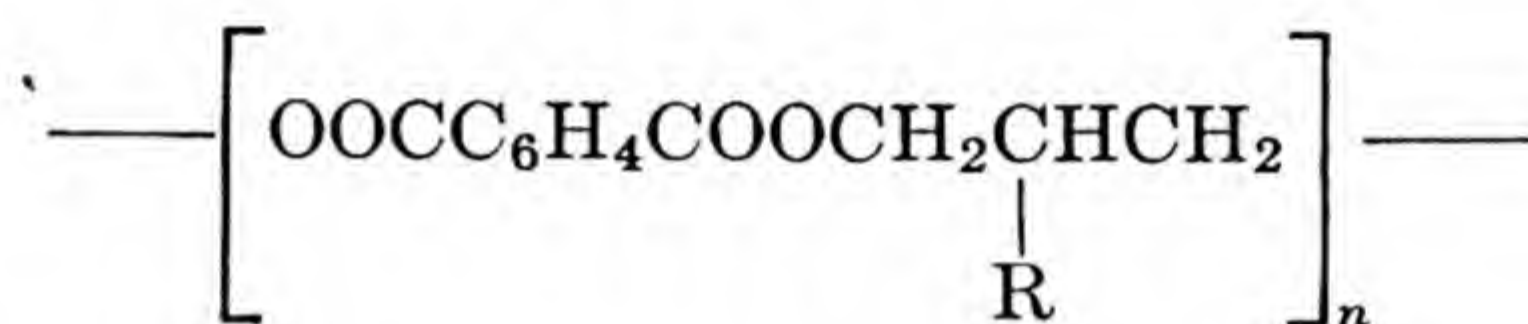
where R is a group such as $C_{18}H_{33}COO$. However, this representation indicates a completely linear polymer that is not ordinarily produced, as the phthalic acid is also capable of reacting with the third hydroxyl group in such a manner that it forms cross linkages. In any case, such a representation of the structure is probably an oversimplification of the actual complicated results of condensation.

These modified resins are made by adding fatty acids such as the acids from the nondrying oils: stearic, palmitic, oleic. As a rule the purified acids are used instead of the oils, as it is difficult to incorporate the oils directly. The drying oils or oil varnishes are also used to modify these resins. Soybean, linseed, tung, castor, and fish oils have all been used. Another type of modification is attained by incorporating rosin or natural or synthetic resins.

The properties of the oils affect the resin coating. Linseed oil dries well to hard films but has a tendency to discolor. Tung oil dries rapidly and produces almost waterproof films. Soybean oil results in slower drying softer resins that have superior color retention. Fish oil has satisfactory drying characteristics but imparts poor color and odor. Castor oil can be used to produce either a nondrying plasticizing resin or an air-drying type with very desirable properties. In order to make the second type, the nondrying castor oil is dehydrated by a heat-treatment, becoming unsaturated and acquiring drying properties. Other nondrying oils, such as cocoanut oil, are useful in the manufacture of resins that have excellent color

retention but require blending with a harder resin, such as urea-formalde-hyde, to provide the necessary drying and hardness.

Although the resins are mixed esters, the term "per cent of alkyd in the resin" or "alkyd portion" is used in contrast to the "oil portion." As the amount of the alkyd portion or alkyd per cent is varied, the properties of
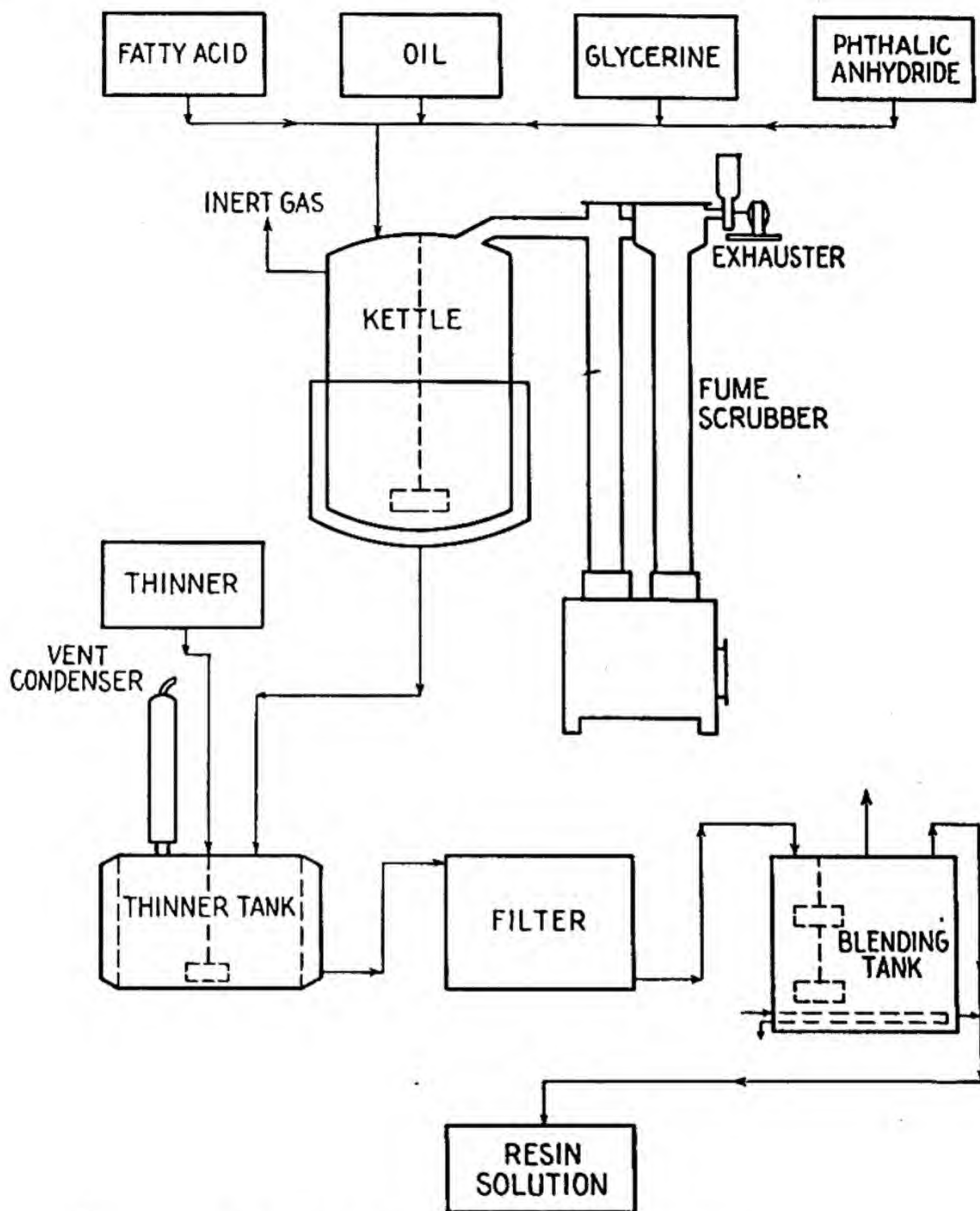
FIG. 74.—Flow sheet for alkyd resins.

the resin are changed. This one factor determines the rate of drying, the durability, the solubility, the compatibility, and other properties of the resin.

The actual manufacturing process is comparatively simple. Stainless steel or aluminum kettles are usually used. They are either electrically heated or direct-fired and are equipped with agitators, special reflux condensers, means of applying an inert atmosphere and vacuum. The raw

materials are heated to 200 to 250°C., which is the reaction temperature. The time required to complete the reaction varies from 5 to 16 hr. (see Fig. 74). At the end of this period, the resins are usually incorporated in solvents such as toluene, xylene, or coal-tar naphthas and sold as solutions. Some of the paint companies add the molten resin directly to varnish oils. In other cases, the resin is poured into drying pans and allowed to cool to a hard solid resin.

The alkyds are used for every conceivable type of coating from printing inks to coated fabrics. They are the most widely used resin in durable air-drying outdoor paints and, together with the phenolics and ureas, supply the baking finishes and high-grade enamels and varnishes. They also have some use as adhesives.

Unsaturated Polyesters.—Unsaturated polyesters are produced by condensing raw materials in which the acid or the alcohol or both contain reactive double bonds. The preparation of these esters up to this point resembles that of the alkyds, except that esterification is usually stopped at the point where a viscous liquid polymer is produced suitable for direct application to fabrics or wood as an adhesive for the production of laminates. Since they contain reactive double bonds, polymerization can continue through the double bonds to produce a hard, strong three-dimensional polymer. This final cure can be accomplished at relatively low temperatures and pressures by the use of peroxide catalysts.

At the present time, these resins are used almost exclusively for the production of laminates by the low-pressure molding processes. Their unusual structural strength makes them ideally suited for this purpose. When glass cloth is used as the laminating material, laminates have been produced which have edgewise compressive strengths as high as 45,000 lb. per sq. in. These resins also possess the excellent water and chemical resistance of thermosetting resins and have good dielectric properties and high heat resistance. Their adaptation to the low-pressure molding processes, their high quality, and the variety of possible variations due to the use of different raw materials give promise of offsetting the disadvantage of relatively high cost, particularly where quality products are required.

Another type of polyester, containing only a small amount of unsaturation, forms a class of compounds known as "polyester rubbers." They are high molecular weight linear polyesters that are soft enough to be rubbery and are capable of undergoing a vulcanization reaction. They are prepared by the condensation of dibasic acids with glycols or by the self-condensation of hydroxy acids. A representative structure is indicated by the following type formula:

$$\text{HO}(\text{—R—O—}\underset{\displaystyle \overset{O}{\|}}{C}\text{—R'—}\underset{\displaystyle \overset{O}{\|}}{C}\text{—O—})_n\text{—R—OH}$$
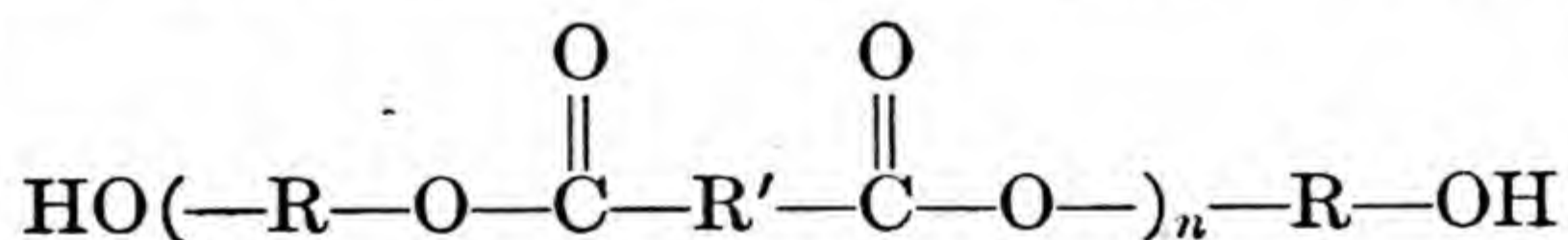
They are made of relatively pure intermediates of known structure.

Raw gums are light-colored, translucent, or transparent resins which in appearance resemble milled natural rubber. They can be compounded on rubber mills with many of the common rubber pigments. When they contain a sufficient amount of unsaturation, they can be vulcanized in the usual manner with sulfur and sulfur accelerators, but benzoyl peroxide is a better vulcanizing agent. Much less unsaturation is required for the peroxide than for the sulfur vulcanization. Peroxide-cured products are practically odorless and thus suitable for many applications where odor is objectionable. The vulcanization can be controlled by the amount of peroxide and the amount of unsaturation built into the molecule.

The properties of this material are determined by the raw materials employed. When long-chain dibasic acids are used in the preparation, products with very low brittle points can be obtained. If a high degree of oil resistance is desired, a short acid with a high concentration of polar groups is chosen.

They have relatively low resistance to alkaline and acid solutions and to steam since the ester is subject to hydrolysis. The electrical properties are inferior to those of natural rubber for insulation purposes, and it is not suitable for tire construction since carbon black interferes with the vulcanization reaction. The outstanding characteristics are high heat and oil resistance and low-temperature flexibility.

Another polyester rubber is produced from vegetable oils. This rubber substitute also possesses good low-temperature flexibility and oil resistance and can be readily processed on rubber machinery. Considerable development work was done on this polyester during the war as a possible rubber substitute for many uses.

POLYAMIDES

The polyamides represent a remarkable development in the fields of synthetic fibers and plastics. This new type of polymer was the result of the endeavors of Walter H. Carothers and his coworkers in this country. It was announced in 1928, and the early 1930's saw the first production of synthetic polyamide fibers possessing strength equal to natural silk and other properties superior to any natural fibers.

In some respects, the polyamides resemble the polyesters in that the most common method of producing them is by condensing two different reactants, each one of which has two functional groups to keep from reacting with the other.

Theoretically, amino acids having an amine group at one end and a carboxyl group at the other could be condensed to give a linear polymer.

$$NH_2RCOOH \longrightarrow \left[-NHRC\underset{\substack{\| \\ O}}{}-NHRC\underset{\substack{\| \\ O}}{}- \right]_n$$
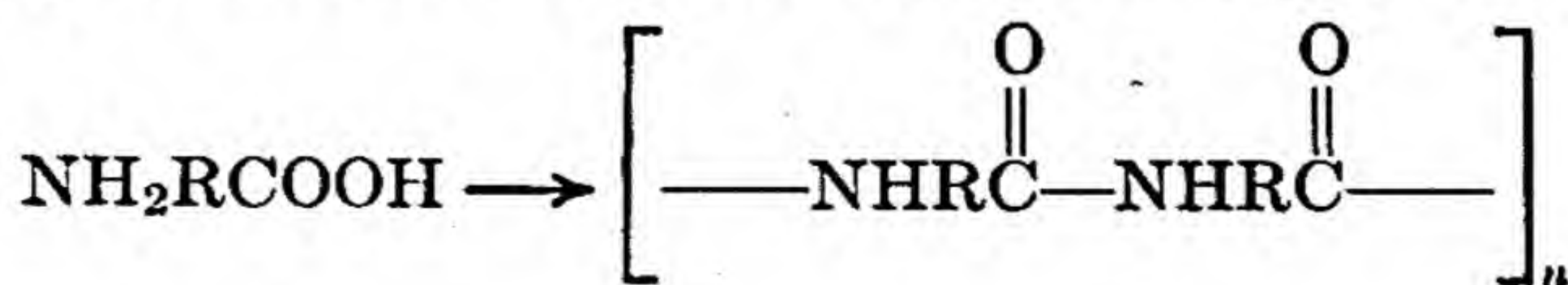
Commercially, the use of amino acids would involve many difficulties. For this reason, diamines and dibasic acids are condensed to give polymers by amide linkages. These polymers have been given the generic name "nylon."

The polyamide in commercial production in the United States at present is made from adipic acid and hexamethylene diamine, which is also derived from adipic acid.

$$HOOC(CH_2)_4COOH + H_2N(CH_2)_6NH_2 \longrightarrow \left[-\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}-NH(CH_2)_6NH- \right]_n$$
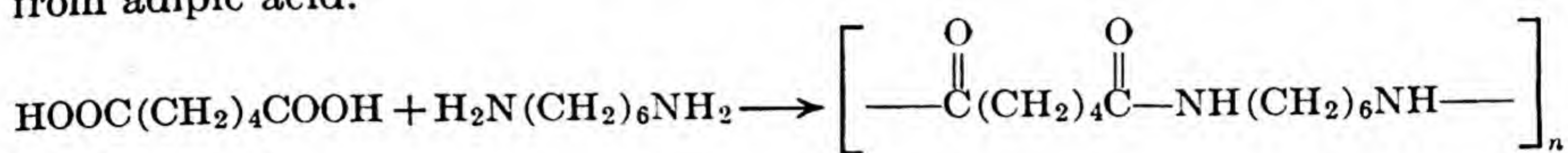
Other diamines and dibasic acids can be used, but this particular nylon gives a product with desirable properties at a reasonable cost.

Germany quickly started the development of nylon fibers and produced three different types during the war. The first type introduced was the same as the one just described. It was known as Igamid A. A second type known as Igamid B was made by the polymerization of ω-caprolactam, used either alone or with the standard Igamid A. It might be noted that when the ω-caprolactam polymerizes by itself by straight addition there is no splitting out of water as in the case of the standard type made from hexamethylene diamine and adipic acid. Fibers made from the caprolactam are claimed to be superior for many textile uses in that they have a higher moisture absorption. ω-Caprolactam has the following structural formula:
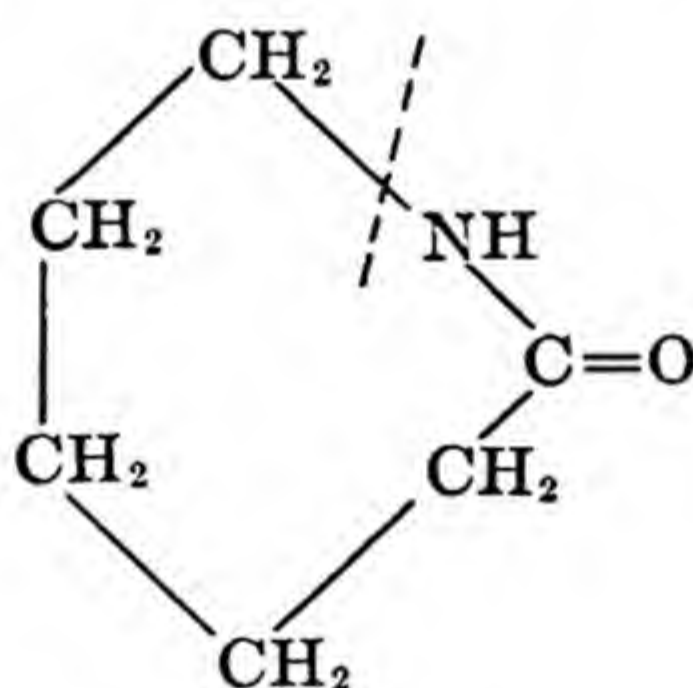
When it polymerizes, it breaks the linkage indicated by the dotted line, giving a linear polymer having the individual molecule as a unit of structure.

A third type that was developed in Germany was a polyurethane made from hexamethylene diisocyanate, $OCN(CH_2)_6NCO$. The isocyanate group has the ability to react with other bifunctional compounds having hydrogen atoms replaceable by a base. For example, it may react with a diamine or a dihydroxy compound to form, respectively, polymers of the following unit structures:

$$[--NHOCHN(CH_2)_6NHCO-NH(CH_2)_6--]_n$$

$$[--OOCHN-(CH_2)_6NHCOO(CH_2)_6--]_n$$
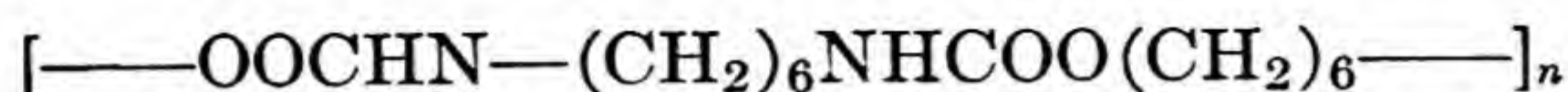
It will be noted that this type of polymer is made by addition. The diisocyanates are very useful reagents in producing cross linkage, for example, in partly hydrolyzed cellulose acetate fibers.
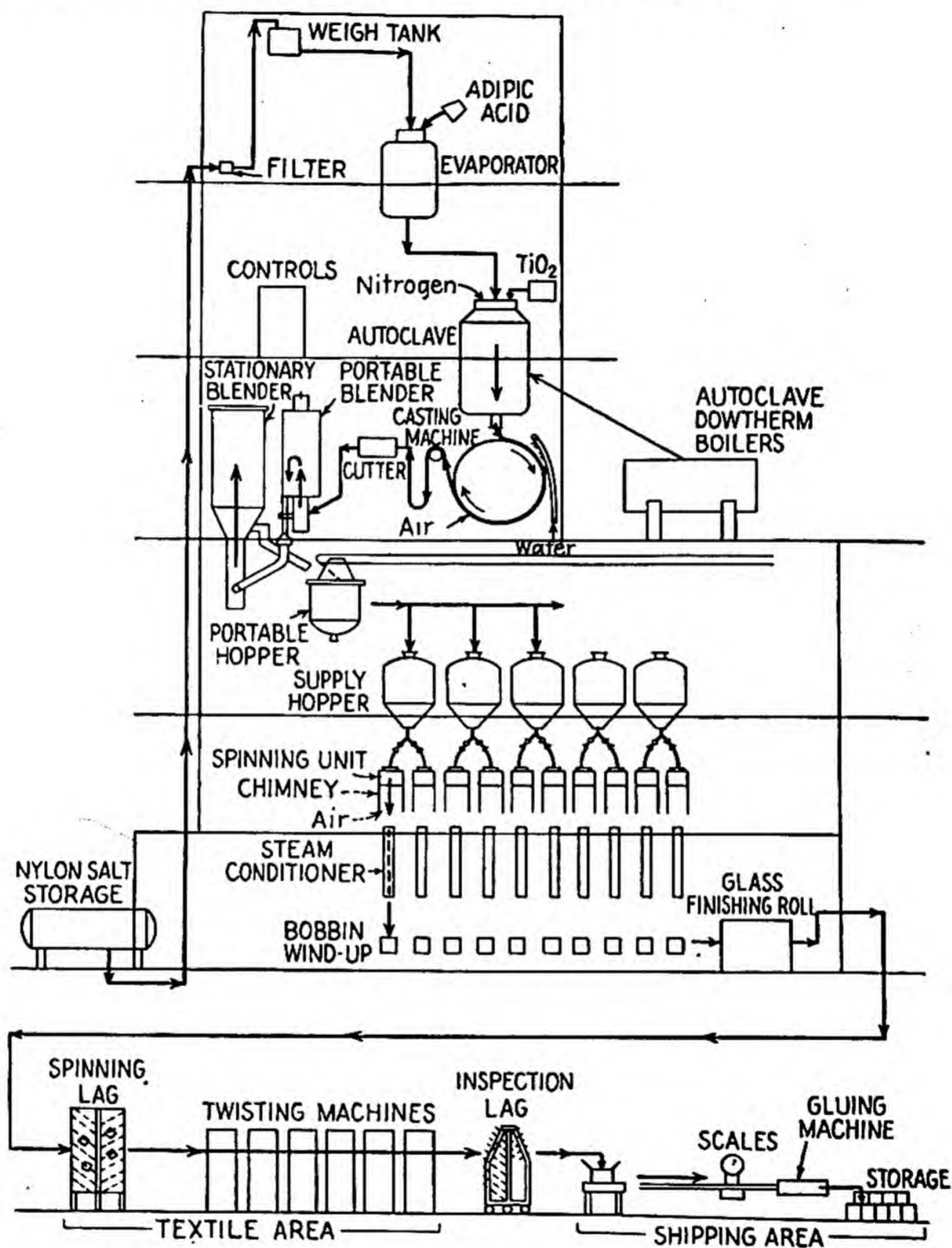
Fig. 75.—Flow sheet for nylon. (*Chem. and Met.*)

In producing the standard type of nylon, adipic acid and hexamethylene diamine are combined to form a salt which is charged into an autoclave where polymerization is carried out. Stabilizers are added to control molecular weight and viscosity. In this reaction a long-chain linear polymer is formed with a molecular weight of 10,000 or higher (see Fig. 75). After polymerization, the molten nylon is extruded as a ribbon onto a

chilled roll, and the ribbon is cut into small chips—a convenient form for storing, handling, and blending various batches to ensure uniformity.

If nylon fibers are to be formed, the chips are charged into the hopper of the spinning unit and drop onto a specially designed heated grid where the polymer melts. The melt is pumped and metered by specially designed pumps and finally filtered through filter packs before passing through the spinnerette to form filaments. All parts of the equipment must be maintained at a temperature above the melting point of the polymer, and a blanket of inert gas must be maintained to prevent any undesirable effects from oxidation at the elevated temperature. The filaments harden quickly as they are exposed to the air outside the spinnerette and are wound up on bobbins operated at a thread speed of over 2,500 ft. per min.

At this stage, the filaments are in an undrawn condition. They are then drawn out to about four times their original length. During drawing, each filament "necks down" and takes a smaller diameter, and after drawing it retains this new dimension permanently. The fiber becomes highly oriented and has a different physical structure, as can be shown by X-ray diagrams. It now has extremely desirable textile properties, particularly a high degree of elasticity, combined with a tensile strength greater than that of any of the commonly used textile fibers.

The first nylon hosiery turned out, made by ordinary silk-hosiery techniques, showed marked defects. The most serious was excessive wrinkling of the stockings during the dyeing operation, and this wrinkling could not be overcome by any subsequent pressing or boarding operation. The wrinkles appeared to be permanently set in the stockings. This difficulty was completely overcome by placing the stockings, before dyeing, on a form and subjecting them to a steam treatment at high temperatures. This treatment, known as "preboarding," sets the stitch and the form of the stocking and permits subsequent dyeing without trace of wrinkling.

Nylon has only moderate resistance toward mineral acids and strong oxidizing agents, but it is practically inert against alkalies, aliphatic, aromatic, and halogenated hydrocarbons, organic acids, ketones, alcohols, and carbon bisulphide. Solvents include phenol, cresol, cresylic acid, formic acid, and xylenol.[1] Nylon is rapidly disintegrated by cold concentrated nitric acid, while 10 per cent sodium hydroxide at 85°C. for 16 hr. does not harm it.

Melting point of nylon 66 is 253°C. The density as compared with other yarns is low:

Nylon 66 . . . . 1.14
Silk 1.30
Viscose rayon 1.52
Acetate rayon 1.30

[1] *Chem. & Met. Eng.*, **52**, 97 (1945).

At present, two kinds of nylon yarn are produced: standard and high tenacity. Standard yarns have a tenacity of 4.5 to 4.8 g. per denier and an elongation of 18 to 22 per cent before breaking. High-tenacity yarns have a tenacity of 6 to 7 g. per denier and an elongation of 11 to 17 per cent before breaking.

Nylon has a higher tenacity than silk. This point is emphasized by the fact that the wet strength is about 88 per cent compared with the pronounced weakening of other fibers:

Fig. 76—Various products made from nylon. (E. I. du Pont de Nemours & Co.)

Fiber	Tenacity, g. per denier	
	Dry	Wet
Nylon 66...................................	5	4.5
Silk......................................	4.6	3.9
Viscose rayon.............................	1.8	0.9
Acetate rayon.............................	1.5	1.0

The water absorption (at 60 per cent relative humidity) is as follows:

	Absorption, per cent
Nylon 66	3.5
Silk	11.0
Wool	13.0
Viscose rayon	12.0
Acetate rayon	6.5

FIG. 77.—Nylon plastic products. (*E. I. du Pont de Nemours & Co.*)

Nylon can be fabricated into many types of articles in addition to textile yarns. By methods somewhat similar to the extrusion of fine textile filaments, it forms monofilaments of larger diameter, which are superior to hog bristles (see Fig. 76). They are widely employed in both toilet and industrial brushes and are also used as tennis and badminton-racquet strings, surgical sutures, fishing leaders, and similar products where a high degree of strength, toughness, and elasticity are demanded. It is also employed for many special fabrics for such purposes as parachutes and powder bags. Its low water absorption, high strength, and complete re-

sistance to fungi make it suitable, although expensive, for high-strength rope. The same qualities indicate that it may have other marine uses such as sails and canopies.

Nylon is also produced as a molding powder and merits consideration where the need is for toughness, high softening temperature, and molding by the injection method (see Fig. 77). Nylon is thermoplastic in the sense that it can be softened by heating, made rigid by cooling, and re-softened by heating again, but it does not show the same degree of increase in creep and decrease in strength, as the temperature is raised, as do other thermoplastics. In common with nylons of the types used in yarns and filaments, FM-1 nylon shows a marked tendency to crystallize. For that reason its behavior at its softening temperature is different. Although FM-1 nylon does not completely collapse as do other thermoplastics until its temperature has been raised to about 450°F., it should not be subjected to temperatures above 275°F. under load.

Among molding powders of high impact strength, nylon has the outstandingly low density of 1.14 g. per cc. as compared with the 1.27 to 1.56 of cellulose acetate and the 1.4 of fabric-filled phenolics. The low density in some measure offsets the present high cost.

PROPERTIES AND USES OF NYLON

Advantages:

    Extreme toughness
    High strength
    High heat resistance

Disadvantages:

    High molding temperature
    Poor solubility

Common uses:

    Hosiery
    Rope
    Textiles
    Bristles
    Tennis-racquet strings
    Molded articles

PART V

POLYETHENIC RESINS

This entire class of polymers is formed by the polymerization of monomers through ethylenic carbon-double-bond-carbon linkage. For this reason it is convenient to regard the monomers as derivatives of ethylene, although many of the compounds involved would not be so regarded in the best practices of organic chemistry. This class of polymers has also been denoted as polyvinyls, although the definition of the monomeric vinyl compound is open to dispute and some of the polymers included here are definitely not derivatives of vinyl compounds as we ordinarily think of them. The most accepted definition of a vinyl compound is one having

the structure $CH_2{=}C{\overset{\displaystyle X}{\underset{\displaystyle Y}{\diagup}}}$, where X and Y may both be hydrogen or one

may be hydrogen and the other an alkyl, aryl, or one or more negative atoms or groups, such as a halogen, hydroxyl, nitro, or acetate. Included in this section are types derived from monomers in which atoms or groups, other than hydrogen, are substituted on both carbon atoms, e.g., the fumaric acid esters. These are definitely not vinyl compounds, as just defined.

Polyethylene is the typical polymer in this class and, as far as structure is concerned, the other polymers form the same type of saturated chains in which one or more hydrogen atoms on one or both carbon atoms of each recurring ethylene group have been replaced by other groups. Thus polyethylene is formed from ethylene as follows:

$$CH_2{=}CH_2 \longrightarrow [{-}CH_2CH_2{-}]_n$$
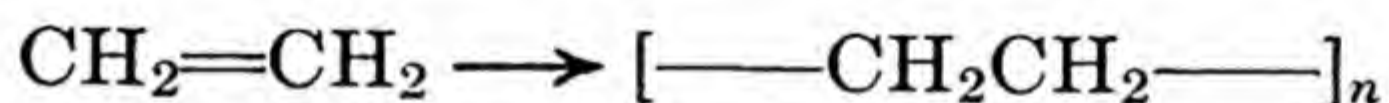
If one of the hydrogen atoms on ethylene is replaced with chlorine, vinyl chloride polymerizes to polyvinyl chloride.

$$CH_2{=}CHCl \longrightarrow \left[\begin{array}{c} {-}CH_2CH{-} \\ | \\ Cl \end{array} \right]_n$$
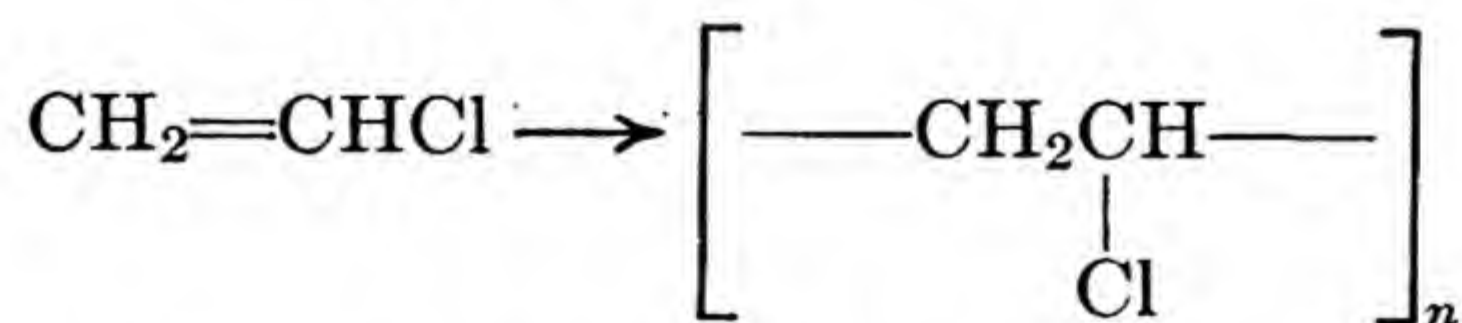
These resins all polymerize by typical addition polymerization and form chain-type polymers. This is the typical thermoplastic structure, so all the members of this class are thermoplastic unless deliberately altered by introducing possibilities of cross linkage through special substituted groups.

Since the polymerization is of the addition type it is, in general, catalyzed by peroxides and the equipment and processes employed are of the same general type for many of the polymers.

The properties of the various polymers and plastics produced from resins of this class vary over a wide range, extending all the way from soft, tacky adhesives to hard solids. Most of the polymers can be compounded into rubberlike products that can be used as rubber substitutes but are not true elastomers. In general, their rubberlike qualities are due to plasticizers and methods of compounding rather than to elasticity of structure. Another property common to most members of this class is their clear white color and comparatively high clarity.

The groups that are introduced into the ethenic structure in place of hydrogen are as follows:

1. Monosubstitution
    a. Hydroxyl and alkoxy
    b. Chloro
    c. Acetate
    d. Phenyl
    e. Chlorophenyl
    f. Carboxyl
    g. Cyanide
    h. Acetyl
    i. Esterified carboxyl
    j. Amine
    k. Amide
    l. Methylol (substituted)

2. Disubstitution on the same carbon atom
    a. Dichloro
    b. Dimethyl
    c. Methyl and esterified carboxyl
    d. Methyl and acetyl

3. Disubstitution on both carbon atoms
    a. Coumarone and indene structures
    b. Esters of unsaturated dibasic acids

4. Shared substitution after chain is formed
    a. Acetal linkage between two ethenic groups
    b. Lactone and lactam

POLYETHYLENE

Polyethylene, also called polythene, is a newcomer in the field of thermoplastics, having been first introduced commercially about 1940. The polymerization of ethylene has been the object of considerable research; it requires quite strenuous conditions. Pressures used experimentally have ranged from 1,000 to 12,000 atmospheres, although in commercial prac-

tice the range is 500 to 3,000 atmospheres. Catalysts employed are peroxides, gaseous oxygen, and the alkali metals.

A low molecular weight polymer is prepared by polymerizing in methanol. It is useful as an additive to lubricating oil. Higher molecular-weight products are obtained by polymerizing in benzene or massively without a solvent (see Fig. 78).

Chemical properties are those to be expected from the structure and chemical composition. Solubility in organic solvents is low at ordinary temperatures but increases fairly rapidly between 50 to 70°C. Polythene
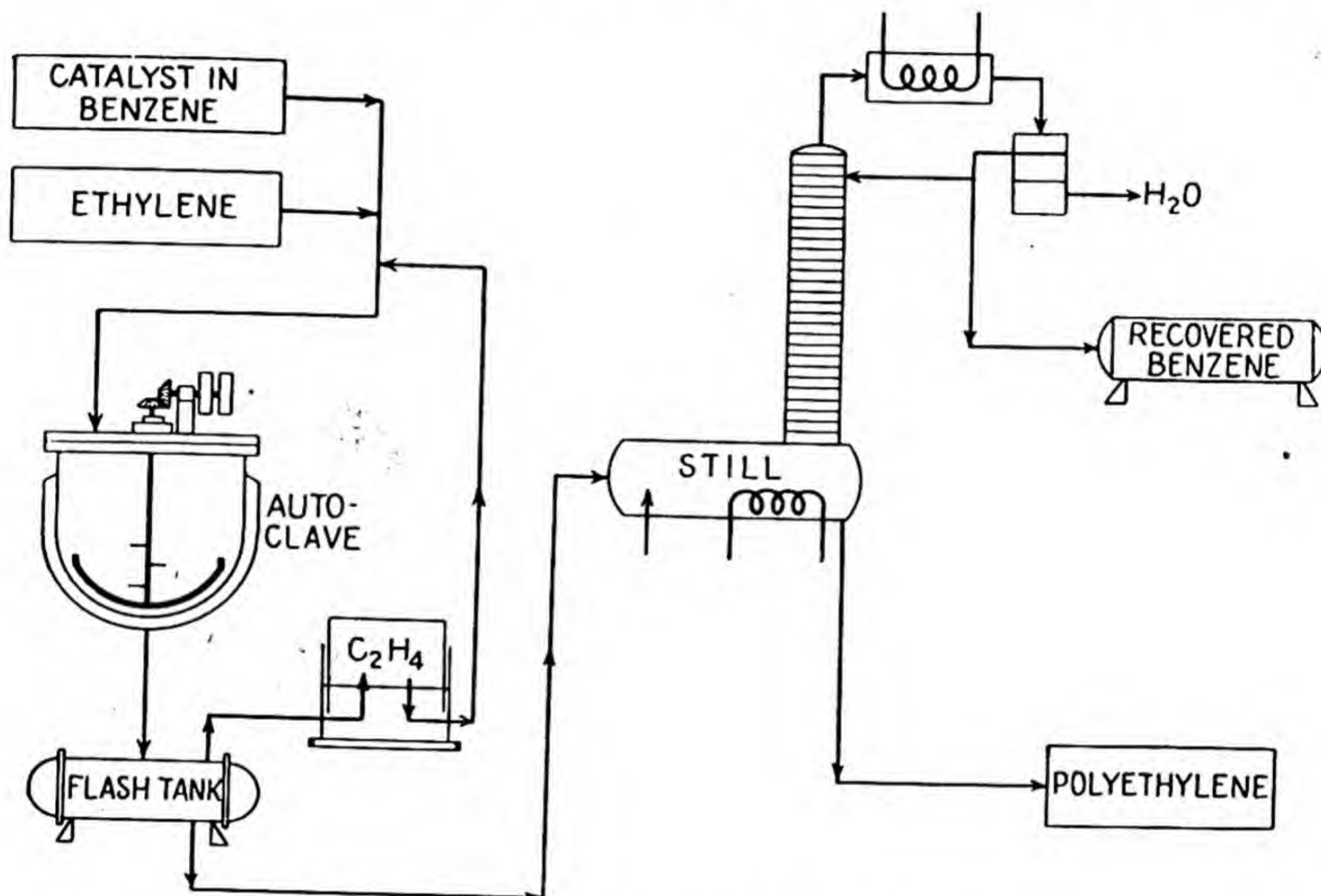
FIG. 78.—Flow sheet for polyethylene.

is unaffected at room temperature by strong acids or alkalies, but is strongly affected by chlorosulfonic acid. At 100°C., it is attacked by nitric and sulfuric acids, but not by hydrochloric acid or 50 per cent caustic soda. It is much less affected by ozone than is rubber. Chlorination produces a series of plastic products ranging from rubbery to hard solids. A tendency toward oxidation can be inhibited almost entirely by the use of anti-oxidants. On heating in high vacuum, polythene remains unchanged up to about 300°C., where breakdown occurs and brittle waxes, greases, and oils are formed.

Physical properties are unique for a saturated hydrocarbon. It is tough, flexible, and possesses great impact strength. Undrawn polythene consists of spherulitic aggregates of ordered regions or crystallites. The size of the spherulites can be varied by thermal treatment. The behavior of poly-

thene under drawing is comparable with that of rubber. The X-ray diffraction pattern shows amorphous as well as crystalline regions. Slight changes in their relative amounts can greatly affect mechanical properties. The most satisfactory plasticizer is polyisobutylene of high molecular weight. A study of the effect of molecular weight distribution on mechanical properties shows that tensile strength, impact strength and flexibility at low temperatures are improved by an increase in the **average** molecular weight.

Polyethylene resins have a rather short softening range of approximately 108 to 112°C. The lower polymers become quite fluid at the latter temperature, but the higher molecular weight material is quite viscous.

Polyethylene is not compatible with many thermoplastics, but can be mixed with rubber, synthetic rubbers, polyisobutylene, and paraffin wax.
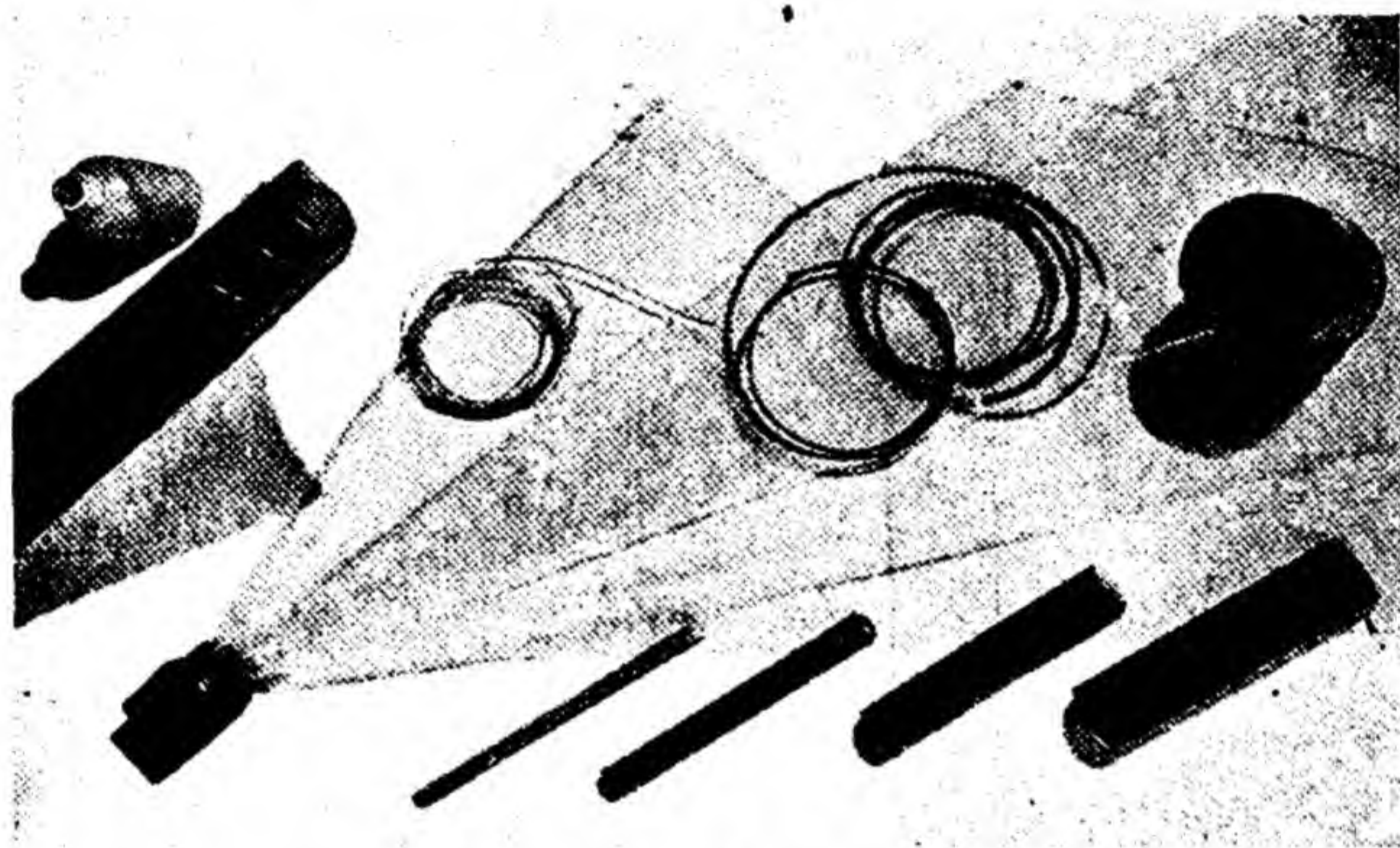
FIG. 79.—Standard shapes made from polyethylene.   (*Plax Corp.*)

Mixtures with polyisobutylene are of particular interest since they have electrical properties almost identical with those of pure polyethylene, and the polyisobutylene acts as a plasticizer to produce a softer and more flexible product especially at low temperatures. Quantities up to 50 per cent may be added, and small amounts of paraffin wax, of the order of 15 per cent, may be added without seriously affecting the electrical or mechanical properties.

Polyethylene can be extruded from the standard type of rubber screw extrusion machine (see Fig. 79). It is essential, however, that the barrel should be heated to at least 115°C., and die temperatures up to 160°C. are required for extruding the stiffer grades. It is easily injection molded, using a die temperature of 160 to 220°C. according to grade. In compression molding it is important to reach a temperature of at least 115°C. Too low a temperature sometimes gives apparently satisfactory moldings, which, however, rapidly become very brittle and cheesy. The shrinkage

is high, averaging 0.018 in. per in. for injection molds and 0.011 in. per in. in a positive compression molding.

Its outstanding properties are flexibility and toughness over a wide range of temperatures, unusually good moisture and chemical resistance, and excellent electrical properties. At the present time its chief use is for wire and other electrical insulation, but its high chemical and moisture resistance suggest possible applications to chemical equipment (see Fig. 80).

FIG. 80.—Special products made from polyethylene. (*E. I. du Pont de Nemours & Co.*)

The completely fluorinated ethylene, tetrafluoro ethylene, has also been polymerized to produce a plastic material of extremely good chemical resistance. It is very inert to halogen compounds of all types and is particularly valuable as a gasket or packing material for handling the highly corrosive acidic halogen solutions and vapors.

PROPERTIES AND USES

OF

POLYETHYLENE

Advantages:

    Excellent electrical properties
    Excellent chemical resistance
    Excellent moisture resistance
    Good flexibility and toughness over a wide temperature range

Disadvantages:
    High cost
    Low rigidity
    Nontransparency

Common uses:
    Wire and cable insulation
    Gaskets
    Packing

POLYISOBUTYLENE

Polyisobutylene is formed by low-temperature polymerization of iso-butylene.

$$(CH_3)_2C{=}CH_2 \longrightarrow \left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2- \right]_n$$
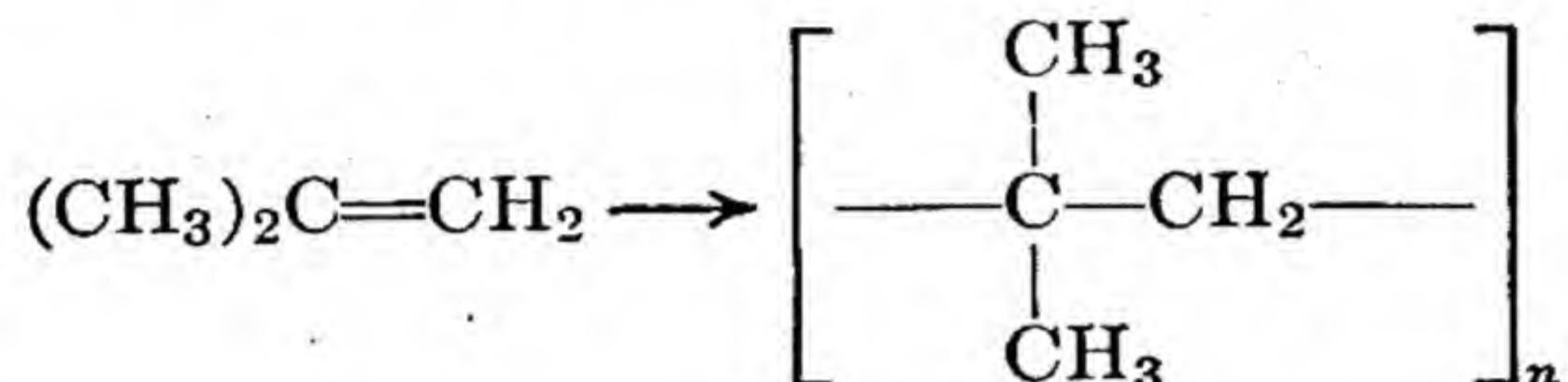
Until the development of polyethylene, it was the only commerically available polymer composed of saturated paraffinic unsubstituted hydrocarbon chains. In many respects it resembles polyethylene but does not have as high a degree of chemical resistance, and its electrical properties are not as good.

Polymerization is accomplished in solution at extremely low temperatures. Temperatures in the range of $-100°C$. are used. The molecular weight or degree of polymerization increases rapidly as the temperature is decreased; polymers having a molecular weight in the neighborhood of 200,000 are formed at $-100°C$. The polymerization is carried out in a solvent composed of a hydrocarbon such as ethylene, with the aid of a boron trifluoride catalyst or anhydrous aluminum chloride dissolved in methyl chloride (see Fig. 81).

Polyisobutylene is frequently classed as a synthetic rubber since most of its applications make use of its rubberlike character and it is usually compounded with rubber and rubber fillers. One of the difficulties encountered in the fabrication of rubberlike articles is the fact that it is not worked or milled easily. This disadvantage was partly overcome in the production of butyl rubber, which is also a polymer of isobutylene but contains about 2 per cent of a diolefin. This small percentage of a diolefin introduces some unsaturation into the finished polymer which tends to make it easier to mill. Butyl rubber is discussed in detail in Part VII.

Polyisobutylene is soluble in hydrocarbon solvents but shows excellent resistance to other chemicals. Nitric acid causes a slight attack, but other acids and bases are without effect. It has excellent resistance to ozone and, like other polymers of this class, has a low permeability toward gases. The saturated character of this material is responsible for many of these

desirable properties, such as resistance to chemicals, ozone, ultraviolet light, and aging. However, disadvantages such as poor workability, cold flow, and poor rebound are also at least partly due to its saturated character.

Mixed with various fillers and other resins it may be compounded into material for gaskets and caulking compounds that are oil-resistant and do
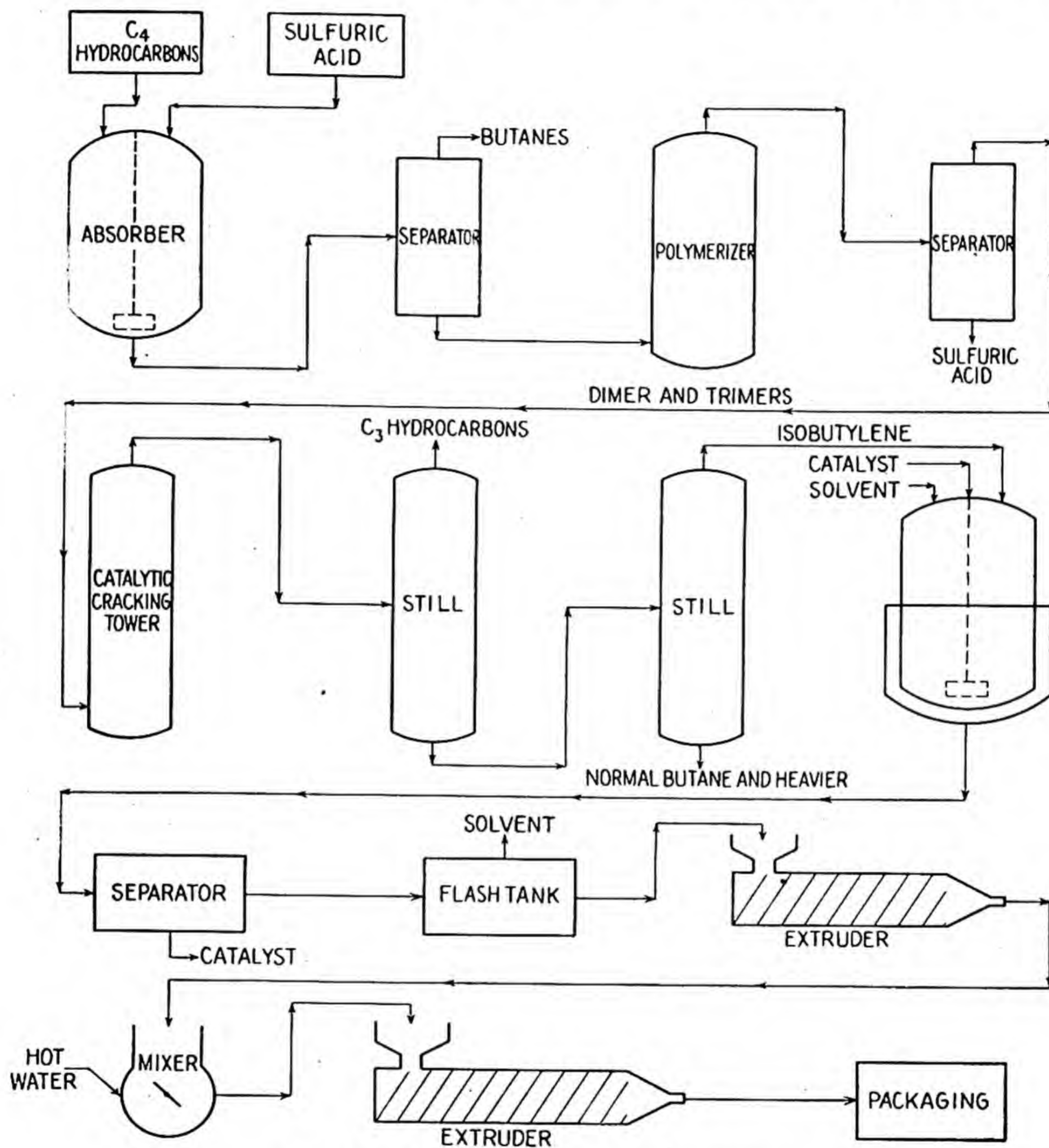
Fig. 81.—Flow sheet for polyisobutylene.

not oxidize. It usually imparts moisture resistance, low-temperature flexibility, and better adhesive properties to formulations with other resins. It is also used as a plasticizer for other resins and waxes.

A variety of grades are produced having a wide range of molecular weights. The lower molecular-weight variety can be used to prevent the thickening of lubricating oils at low temperatures. This material was first

developed in Germany for this purpose previous to the Second World War and was known as Oppanol B. When mixed with wax, the lower polymers improve adhesives and coatings for paper with respect to plastic properties and resistance to moisture.

POLYVINYL ACETATE

The production of vinyl acetate from acetylene and acetic acid was first described in a German patent issued to Klatte in 1912. At that time ethylidene diacetate, which is formed from the same materials, was of interest as a solvent. In 1917, Klatte and Rollette described the conditions for polymerization of vinyl acetate and recommended the use of peroxides to accelerate the formation of the polymer. Commercial production of polyvinyl acetate began in Canada about 1920.

Acetylene is reacted with acetic acid in the vapor phase in the presence of mercury salts forming vinyl acetate.

$$HC{\equiv}CH + CH_3COOH \longrightarrow H_2C{=}CHOOCCH_3$$

Large quantities are produced by this method, and acetaldehyde and ethylidene diacetate are obtained as valuable by-products. The ethylidene diacetate, $(CH_3COO)_2CHCH_3$, is an important source of acetaldehyde and acetic anhydride.

A newer method comprises the reaction of acetylene with acetic acid in the vapor phase, employing an activated charcoal catalyst impregnated with zinc salts. Vinyl acetate is formed in good yields without by-products.

Vinyl acetate polymerizes to polyvinyl acetate.

$$CH_3COOCH{=}CH_2 \longrightarrow \left[\begin{array}{c} {-}CHCH_2{-} \\ | \\ O \\ | \\ O{=}C{-}CH_3 \end{array} \right]_n$$
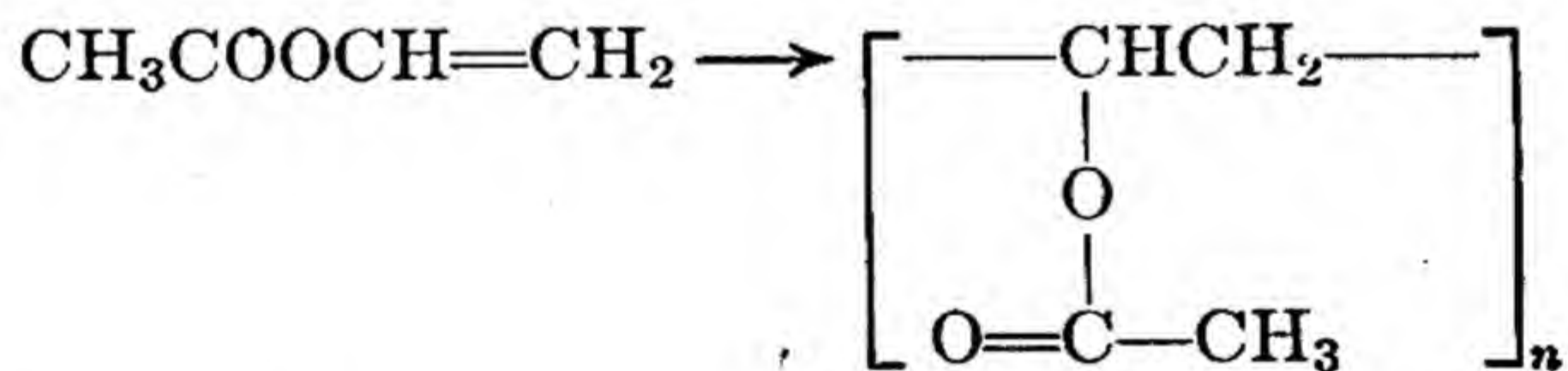
The reaction is usually carried out in a solvent with the aid of peroxide catalysts, although both mass and emulsion polymerizations have been used, particularly in Germany.

A benzene solution of vinyl acetate containing the desired catalyst is introduced into a jacketed kettle. At a temperature of about 72°C., the mixture boils and the vapors are condensed and returned to the kettle. After about 5 hr. at a gentle boil, the reaction mixture is run to a still and the solvent and unchanged vinyl acetate are removed by steam distillation. The molten resin is then either run into drums where it solidifies or extruded into rods and sliced into flakes. The flakes of polyvinyl acetate have a

tendency to form a solid cake so that the resin is usually sold in small packages (see Fig. 82). By a continuous process developed in Germany, the polyvinyl acetate may also emerge in ribbon form (see Fig. 83).

Polyvinyl acetate can be secured in a variety of types of varying degrees of polymerization. Viscosity is used to designate the commercial resins,
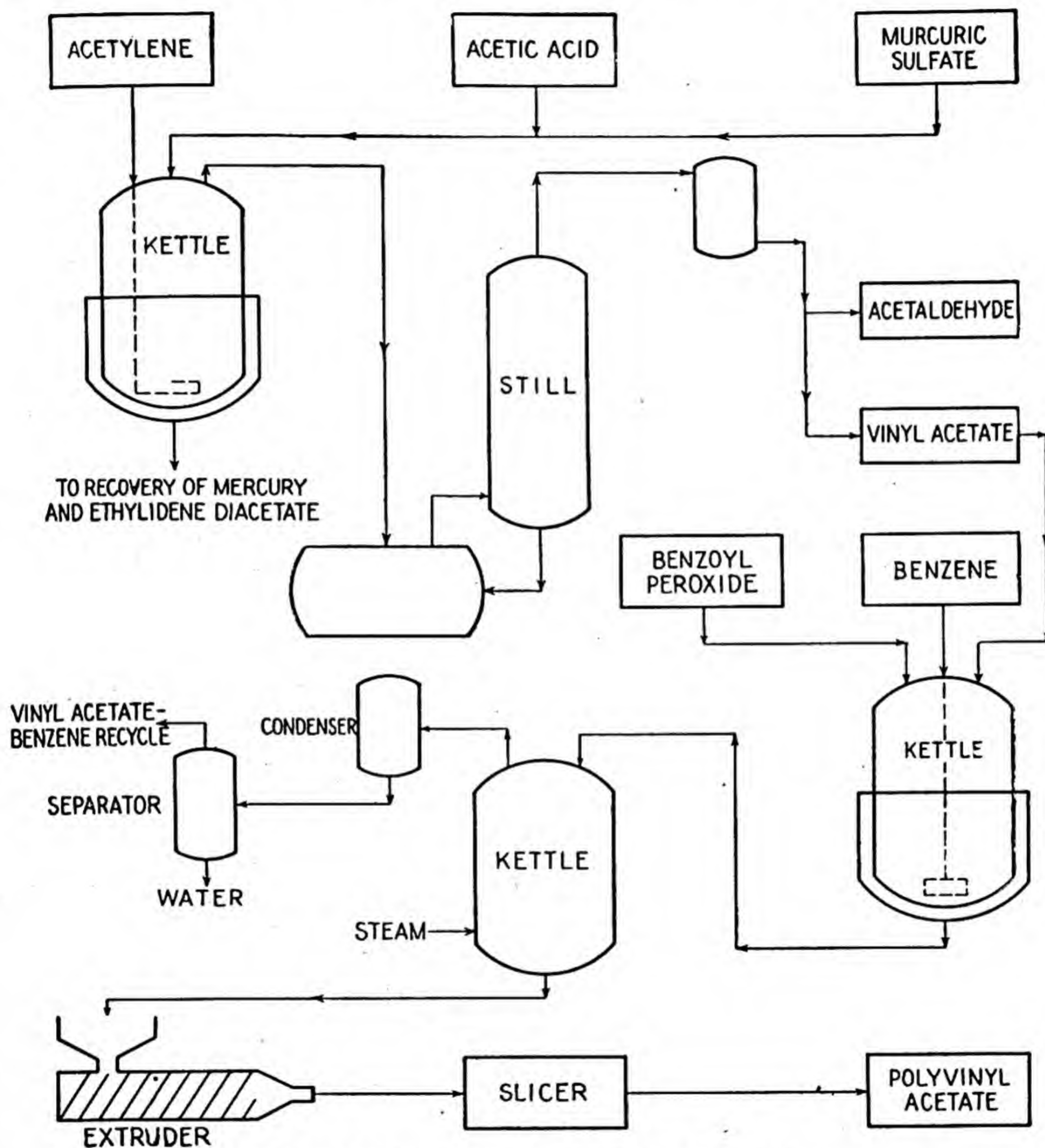
FIG. 82.—Flow sheet for polyvinyl acetate.

and 2.5-, 7-, 15-, 25-, and 60-centipoise types are available. The 2.5- and 15-centipoise varieties are supplied in solution in acetone.

Polyvinyl acetates are colorless, odorless, tasteless, and thermoplastic. The softening point and viscosity increase with the degree of polymerization, although they never attain the hardness of other resins of this class. They are soluble in many solvents and compatible with many of the con-

densation resins as well as with natural resins. Their properties of compatibility, durability, resistance to abrasion, and rust inhibition make them useful for surface coatings. Added to nitrocellulose lacquers they improve the adhesion, luster, and toughness.

Polyvinyl acetate is plasticized by most of the common lacquer types of plasticizers such as phthalates, tartrates, phosphates, abietates, and glycollates. It may be plasticized to any degree of flexibility, much less plasticizer being required for flexibility than with cellulose nitrate.

Polyvinyl acetates are soluble in most alcohols, ketones, esters, ether alcohols, glycols, turpentine, and vegetable and mineral oils. They are
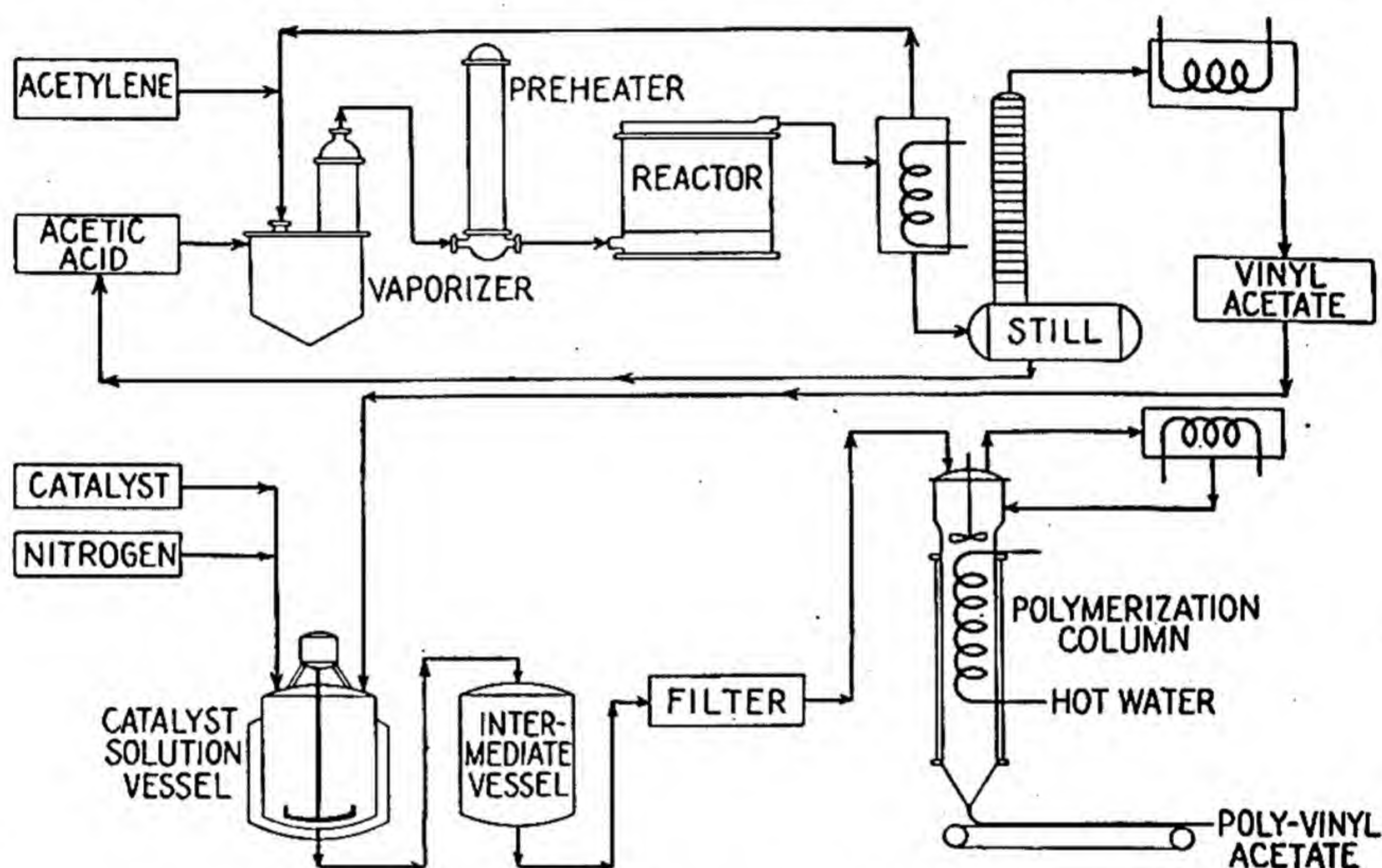
FIG. 83.—Continuous process for polyvinyl acetate polymerization.

insoluble in water, although 5 to 20 per cent of water mixed with the lower alcohols improves the solubility characteristics.

Because of good adherence and tackiness, polyvinyl acetates are used as adhesives for cloth, paper, cardboard, porcelain, metal, mica, stone, wood, leather, glass, and plastic sheets and films. They are used in both solvent and thermoplastic types of adhesives and are particularly good for making paper-to-metal laminations. The adhesive bond that is formed has excellent strength at ordinary temperatures, but the thermoplastic character of this resin restricts its use to conditions where there is no danger of encountering temperatures above 150°F.

The most important use of the polyvinyl acetates is as a raw material for the formation of polyvinyl alcohol. They are not used for molded products because of their softness and tendency to flow, but are important as adhesives and as modifiers of other resins.

Polyvinyl Alcohol.—Polyvinyl alcohol is obtained by the hydrolysis of polyvinyl acetate, since the monomer is the enol form of acetaldehyde and cannot be produced without reverting to the aldehyde form. Thus this resin is not formed by a polymerization reaction, and the degree of polymerization depends primarily on the size of the polyvinyl acetate
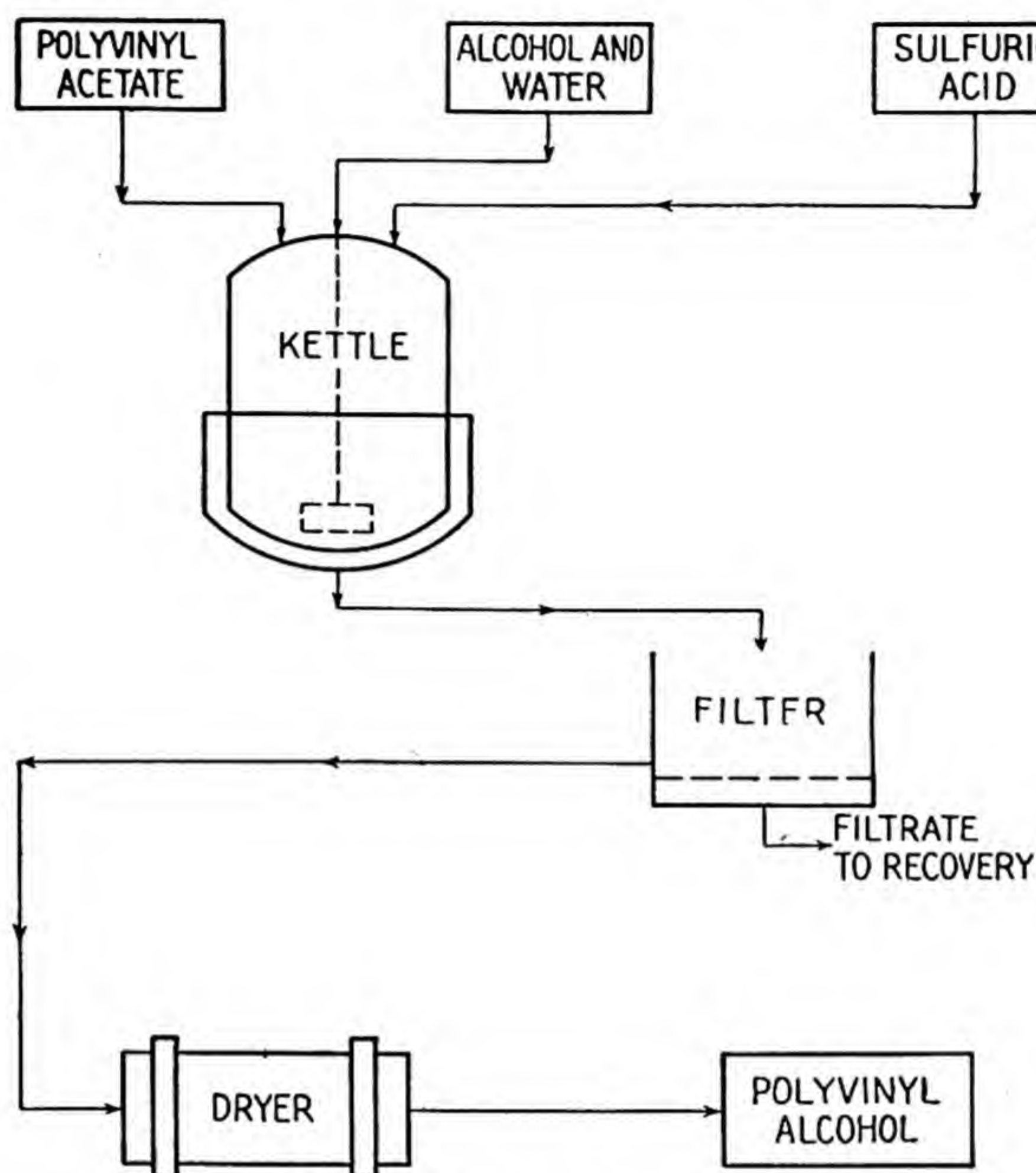
FIG. 84.—Flow sheet for polyvinyl alcohol.

chains. However, the chemical character and the properties of the polymer are altered by the substitution of hydroxyl groups for acetate groups.

$$\left[\begin{array}{c} ---CH---CH_2--- \\ | \\ OCOCH_3 \end{array}\right]_n \xrightarrow{H_2O} \left[\begin{array}{c} ---CH---CH_2--- \\ | \\ OH \end{array}\right]_n$$
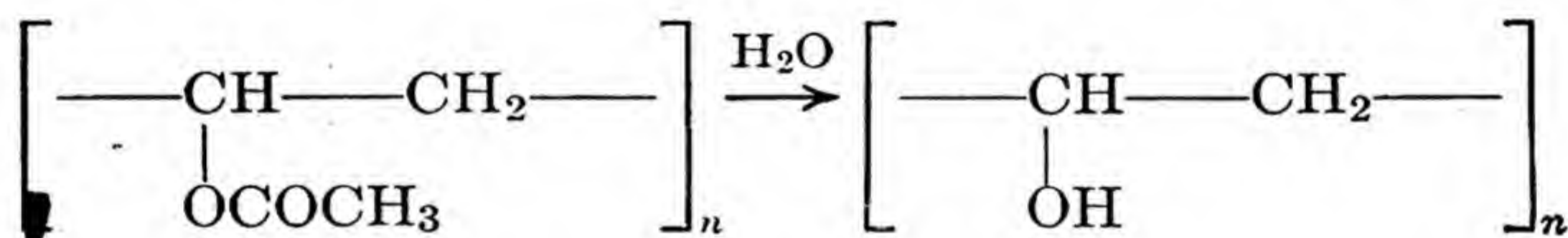
The polyvinyl acetate is dissolved in ethyl alcohol containing some water and introduced into a jacketed kettle together with a small amount of sulfuric acid. The hydrolysis is carried out at moderate pressures to attain the desired reaction temperature. The hydrolysis is not carried to completion, as some acetate groups are always retained in the final product. The precipitated polyvinyl alcohol is filtered off and dried in rotary driers (see Fig. 84).

When the hydrolysis of polyvinyl acetate is carried practically to completion so that less than 5 per cent of the original acetyl groups are retained, the so-called *completely hydrolyzed* type of polyvinyl alcohol is produced. When the hydrolysis is interrupted so that from 50 to 95 per cent of the original acetyl groups remain, the *partly hydrolyzed* type results.

The completely hydrolyzed type of polyvinyl alcohol is soluble in hot water and has good film-forming characteristics as well as good adhesive properties. This type is available in high-, medium-, and low-viscosity grades. Film-forming and adhesive properties of these grades are roughly proportional to viscosity, but the penetration of water solutions into paper, leather, fabrics, etc., decreases with rising viscosity of the polyvinyl alcohol. All grades exhibit excellent resistance to greases and oils.

The partly hydrolyzed type is modified by the presence of residual acetyl groupings. Polyvinyl alcohol containing a small percentage of acetyl is cold-water soluble; a high percentage results in water insolubility. High-, medium-, and low-viscosity grades are available, often in several different saponification numbers in each viscosity class. A variation in saponification number or acetyl content alters the thermoplasticity and moldability of plasticized mixtures, as well as the heat-sealing properties. Some partly hydrolyzed polyvinyl alcohols possess the properties of remoistenable adhesives; others are excellent emulsifying agents, but all are somewhat inferior to the completely hydrolyzed type in grease resistance.

Besides its use as an adhesive, polyvinyl alcohol is used as a sizing or finishing agent for rayon and other textile yarns as well as for greaseproof and other special paper. Since it is soluble in water, it may be applied or removed by standard procedures and equipment.

Plasticized polyvinyl alcohol is extruded in the form of tubing in a variety of diameters for use where high grease and solvent resistance is required or where impermeability to gases is required. The tubing is usually coated with a waterproof lacquer or reinforced with fabric and metal braid which is coated. It can also be molded into sheets and rods or cast into film. Properly compounded, it forms an excellent rubbery sheet or film for gaskets and other applications where its oil-resistant properties are important.

Polyvinyl Acetals.—The polyvinyl acetals are derived from polyvinyl acetate by hydrolysis and condensation with aldehydes. Thus they can be considered a derivative of either polyvinyl alcohol or acetate and, like the alcohol, are not formed by a polymerization reaction. Polyvinyl alcohol reacts with an aldehyde under the influence of heat and an acid catalyst, such as sulfuric or hydrochloric acid. One molecule of the aldehyde condenses with two hydroxyl groups on alternate carbon atoms to produce a six-membered heterocyclic ring with an acetal structure. If butyraldehyde is used a butyral results.

$$—CH—CH_3—CH—CH_2—$$
$$O—CH—O$$
$$C_3H_7$$
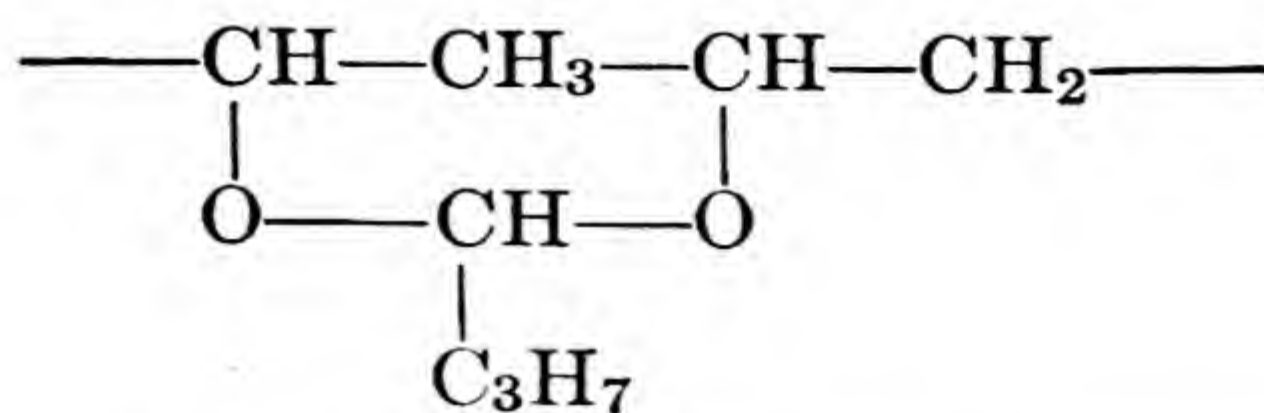
Formaldehyde and acetaldehyde are also used commercially. Most aldehydes are capable of giving this reaction, but the formals and butyrals are by far the most important commercial products.
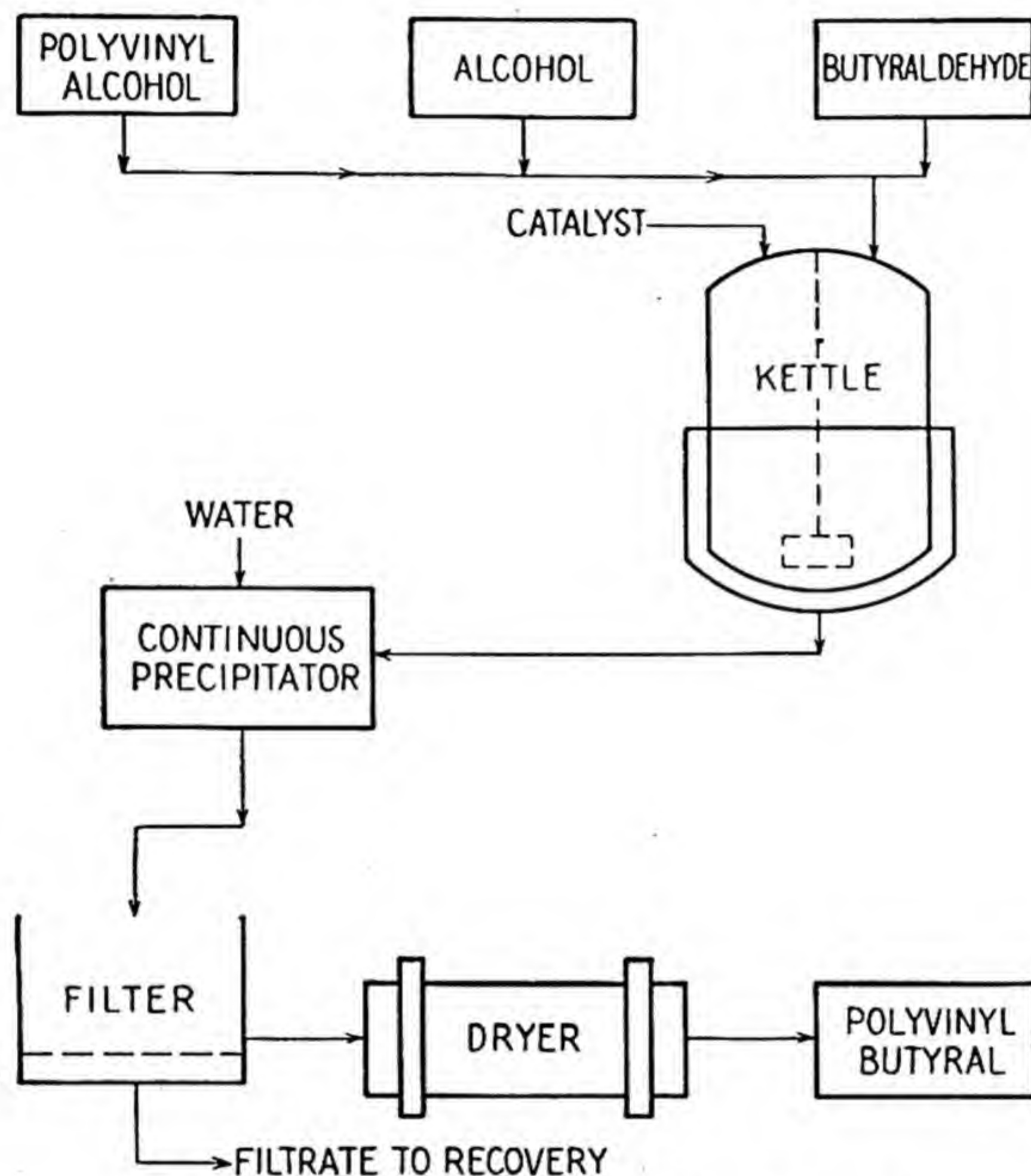
FIG. 85.—Flow sheet for polyvinyl butyral.

The manufacturing process varies, depending on the aldehyde employed. In the production of the butyral, solid polyvinyl alcohol is added to an alcoholic solution of butyraldehyde containing an acid catalyst in a jacketed kettle. As the reaction proceeds, the butyral dissolves in the alcohol. At the end of the reaction it is precipitated with excess water, filtered, washed, and dried (see Fig. 85).

If the formal is being produced, the hydrolysis of the acetate and the reaction of the resulting polyvinyl alcohol with formaldehyde is carried out simultaneously in the same reaction kettle (see Fig. 86). The formal is insoluble in the alcohol solution so the precipitation step is eliminated.

Neither the hydrolysis nor the condensation is carried to completion because the presence of some acetyl and hydroxyl groups in the final resin

gives it desirable properties. The fact that residual acetate and hydroxyl groups remain in the polymer makes the properties of the resin depend on (1) the aldehyde used, (2) the percentage of residual groups remaining, and (3) the degree of polymerization of the original polyvinyl acetate.

As would be expected, the polymers having more residual hydroxyl groups are less water-resistant and less compatible with other resins and plasticizers. They are, however, extremely tough with high impact resistance and good extensibility. The polymer of this type, containing the
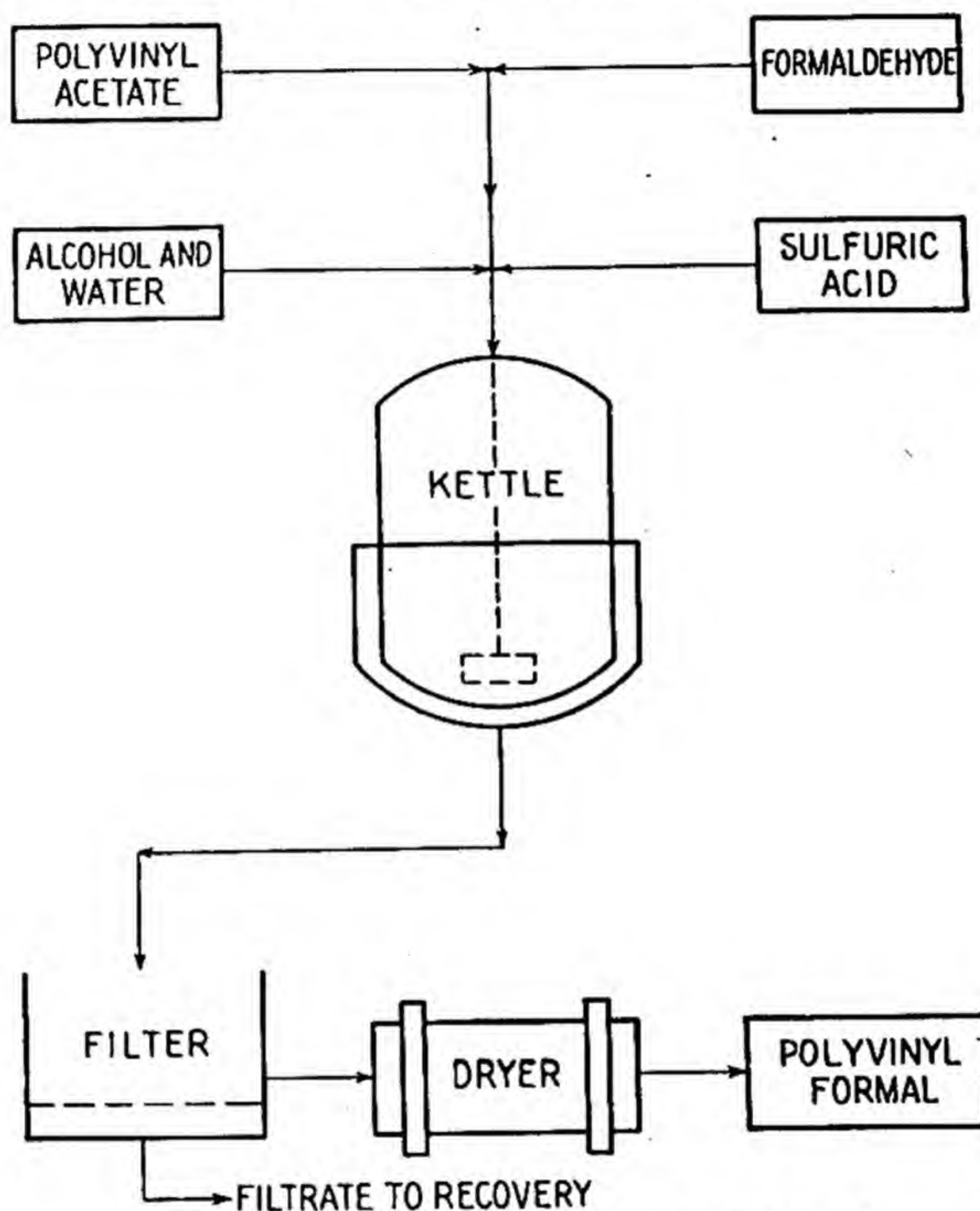
FIG. 86.—Flow sheet for polyvinyl formal.

butyral group, forms the plastic interlayer in safety glass. In this application it is unexcelled in physical properties and has a much longer life when exposed to sunlight and water vapor than the cellulose derivatives that have been used. The properties that make this plasticized polyvinyl butyral resin sheeting so adaptable for use as a safety-glass interlayer are its great extensibility, toughness over a wide range of temperatures, stability toward light and heat, relative insensitivity toward moisture (eliminating edge sealing), and good adhesive qualities. It is also a good thermoplastic adhesive for rubber, paper, wood, and glass.

Polyvinyl butyral can be cross linked by the addition of other resins to acquire thermosetting properties. This reacted form of polyvinyl butyral

is used in coating fabrics to make them waterproof for use as raincoats and tarpaulins. These modified resins make excellent waterproof coatings for severe outdoor use, since they are not affected by wide ranges of temperature and do not become tacky or brittle even under extreme conditions. They also are excellent adhesives and bonding agents.

The acetals can be worked on rubber machinery to produce films and coatings and can be extruded to give flexible tubing. They are not considered a rubber substitute since their recovery after extension is very slow, but are used for soft flexible gaskets and diaphragms where rubber is not suitable.

Polyvinyl formal resins are largely used as a base for an insulating enamel for wire. Such an insulation is tough and water-resistant.

<div align="center">

PROPERTIES AND USES
OF
POLYVINYL ACETALS

</div>

Advantages:

    Very tough
    Good extensibility
    Properties retained over wide temperature limits
    Good adhesion
    Good weathering resistance
    Good moisture resistance

Disadvantages:

    Low softening point (140°F.)
    Relatively high flammability
    Mediocre molding qualities
    Low chemical resistance

Common uses:

    Safety-glass interlayer
    Tubing
    Waterproof coating for textiles
    Insulating enamel
    Molded articles

POLYVINYL CHLORIDE

As early as 1838, Regnault[1] observed the formation of a white powder when sealed glass tubes of vinyl chloride were exposed to sunlight. Baumann[2] polymerized the vinyl halides to white solid masses, "unaffected by solvents or acids." Thus, although these resins were discovered over 100 years ago and the fact that they were inert to chemicals was recognized over 70 years ago, the significance of the reaction and the possible commercial utilization of their properties was not commercially developed until

[1] REGNAULT, M. V., *Ann. chim. phys.*, **69**, 157 (1838).
[2] BAUMANN, E., *Ann.*, **163**, 308 (1872).

1930. Their use increased steadily until the general shortage of materials occasioned by the Second World War caused a rapid expansion in their production both for war uses and as a substitute for scarcer materials. Production in the United States has been estimated as high as 110 million pounds for 1945, and recent information coming out of Germany indicates that polyvinyl chloride played an extremely important roll in that country.

The early development of polyvinyl chloride required a satisfactory and economic process for the production of the monomeric vinyl chloride as well as the discovery of materials and methods for plasticizing. Two methods are now in use for the production of vinyl chloride. In one,
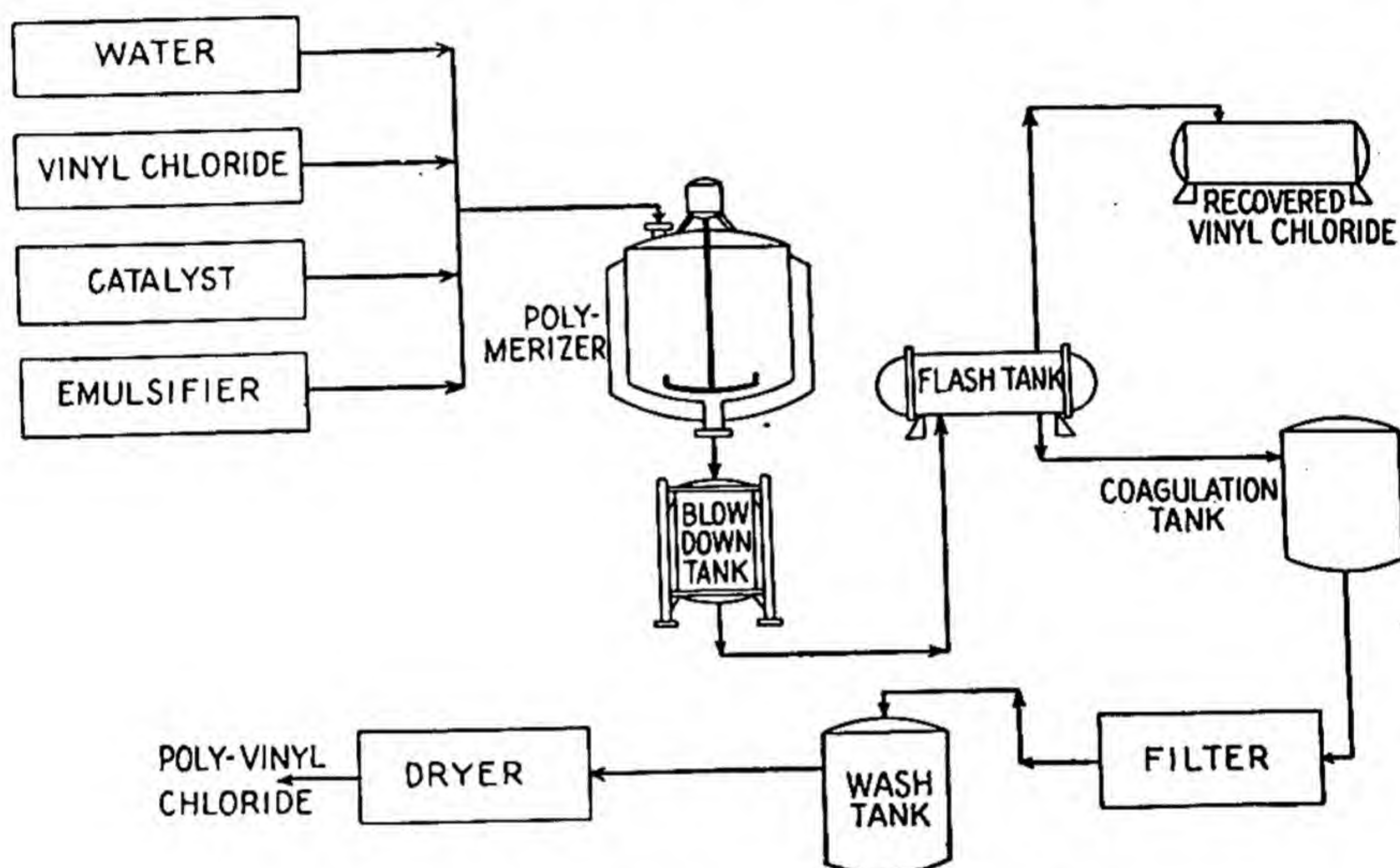
Fig. 87.—Flow sheet for polyvinyl chloride.

acetylene is combined with hydrochloric acid directly in the vapor phase with the aid of a charcoal-impregnated catalyst to give vinyl chloride.

$$CH{\equiv}CH + HCl \longrightarrow CH_2{=}CHCl$$
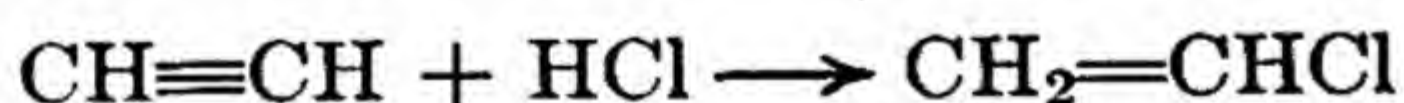
In the other method, ethylene dichloride reacts with sodium hydroxide.

$$CH_2ClCH_2Cl + NaOH \longrightarrow CH_2{=}CHCl + NaCl$$
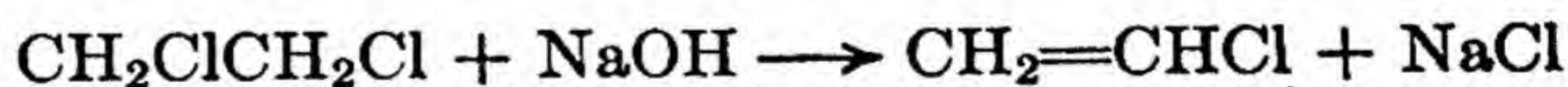
Formerly, vinyl chloride was stored at low temperatures since pressure storage sometimes results in spontaneous polymerization. Recently it has been found that it can be stored at ordinary temperature under an atmosphere of nitrogen.

Polymerization is ordinarily carried out by the emulsion method (see Fig. 87), although both solvent and mass polymerizations have been used.

The reaction is catalyzed by peroxides in a manner similar to the other polymers of this series.

$$CH_2{=}CHCl \longrightarrow \left[\begin{array}{c} {-\!\!-}CHCH_2{-\!\!-} \\ | \\ Cl \end{array} \right]_n$$
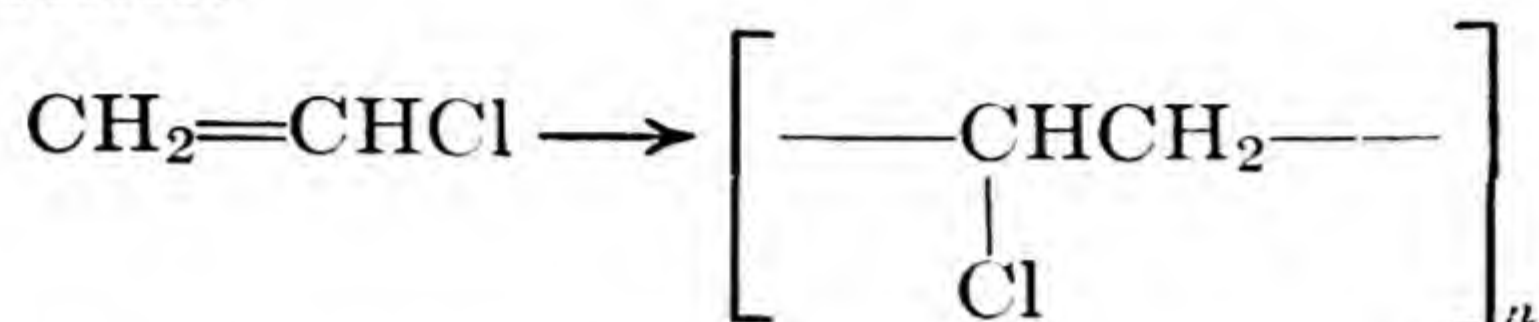
A flow sheet (Fig. 88) shows. the emulsion method with which is combined a new method of spray drying developed in Germany during the
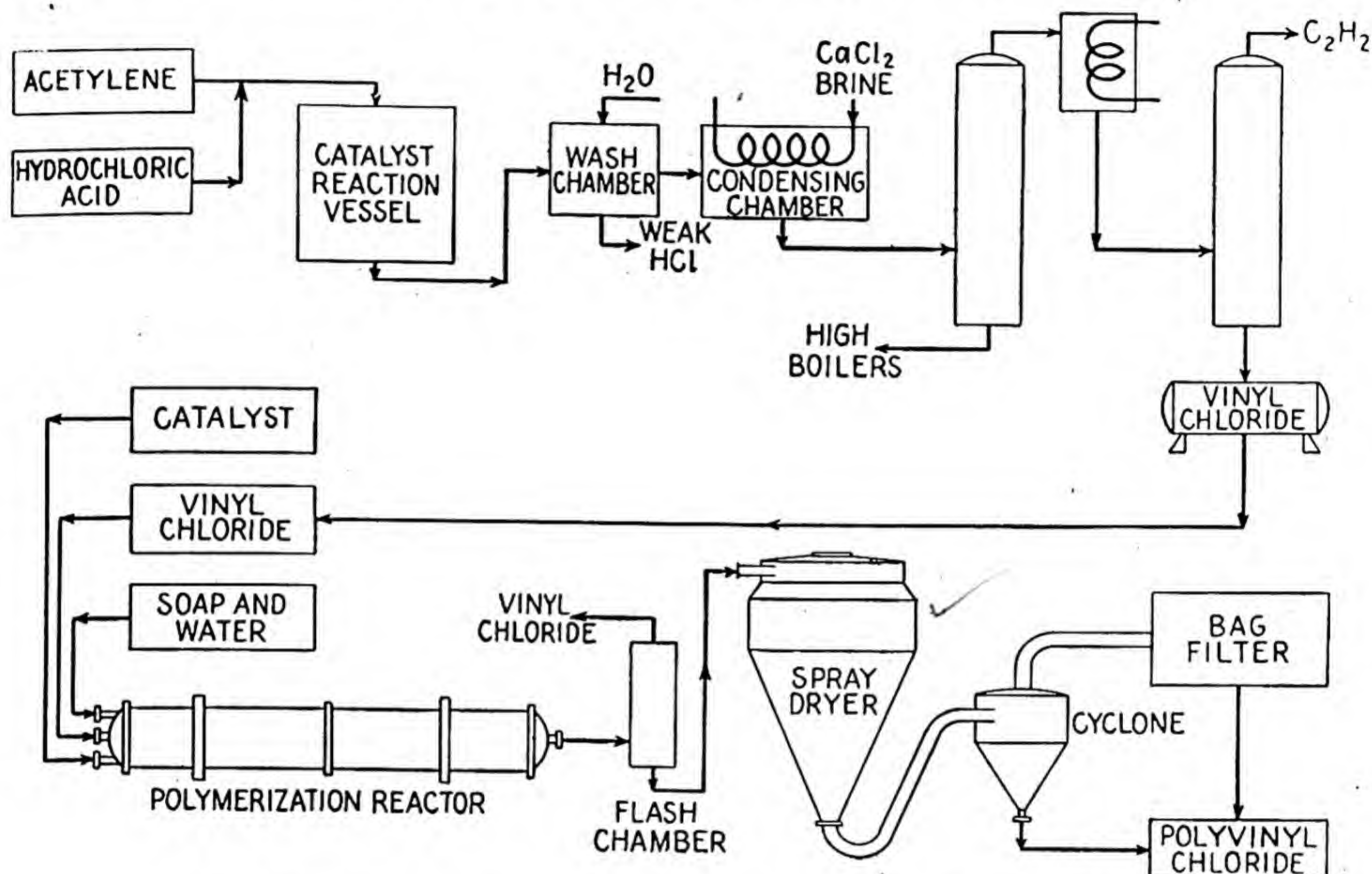
FIG. 88.—German process for the production of polyvinyl chloride.

Second World War. Polymerization is carried out in horizontal rotating reactors made of nickel or enamel lined. A charge consists of the following:

	Pounds
Vinyl chloride	3,500
Water	3,500
Soap	140
Hydrogen peroxide	14

The polymerization is carried out at 45°C. and is 90 per cent complete in 24 hr. The unreacted monomer is vented, and the emulsion is pumped directly to a spray drier and atomized with air heated to 160°C. The finely divided vinyl chloride passes to cyclones in which 90 per cent is' collected and the remainder recovered in bag filters. It is compounded

with plasticizers, stabilizers, and other resins before being worked into final products.

Unplasticized polyvinyl chloride is a hard, horny material that is insoluble in most solvents and not easily softened. If it is mixed while hot with certain plasticizers, it forms a somewhat rubbery material that can be calendered, extruded, and molded. Tricresyl phosphate, dibutyl phthalate, dioctyl phthalate, triglycol ester, and nitril rubber are used as plasticizers. On addition of a plasticizer, the extensibility is increased, but the tensile strength is decreased as the percentage of plasticizer increases. In spite of the loss in strength, many uses require the rubbery character imparted by a high percentage of plasticizer.

Polyvinyl chloride has a tendency to liberate hydrochloric acid, particularly at temperatures approaching the upper limit of serviceability. For this reason it is ordinarily stabilized with such stabilizing agents as lead silicate, basic lead carbonate, or even sodium carbonate.

The required formulating ingredients are usually added in Banbury mixers or by the use of a regular rubber mill. These compounded products can be compressed or injection molded, calendered, or extruded. Coating compositions are made with the use of solvents as well as the water dispersions previously mentioned.

Polyvinyl chloride is nonflammable, practically insoluble in many solvents at ordinary temperatures, moisture-resistant, nontoxic, odorless, and tasteless. Many compounded formulations contain carbon black or pigments and resemble rubber. Like rubber, many different grades can be produced from a very hard material to an almost permanent gel. In its final form it is resistant to light, weathering, flexing, and to most chemicals. It will withstand all the strong acids and alkalies, as well as solutions of nearly all inorganic compounds. It is not resistant to ketones, chlorine, nitro compounds, or gasoline.

The properties of this resin, particularly resistance to aging, chemicals, flexing, and abrasion, coupled with the adaptability of various grades to practically all known processing techniques, result in a very wide range of applications. Except for the cellulose derivatives, it is the most widely used thermoplastic material. The greatest amount of polyvinyl chloride has been used for wire coating or tubing for wire protection. In addition to use as an insulator, tubing of this material has proved popular for chemicals and even for garden hose. Molded products include special gaskets and seals as well as shoe heels, electrical plugs, etc. It does not adhere readily to other surfaces but shrinks on cooling so that objects can be completely coated by dipping them into the molten material, leaving a coating that is "shrunk on." This procedure is used in applying protective (and insulating) coatings to such objects as plating racks for chromic acid plat-

ing baths. The same procedure can be followed in coating wires. Adhesives have been developed to seal polyvinyl chloride to metal so that it can be used for tank linings for acid baths, plating tanks, and chemical storage tanks.

It is also used for moistureproof coatings on fabrics and papers. It can be processed to produce a clear heat-sealable film for moistureproof packaging or sealing. Since it is oil-resistant, it has many applications in the field of gaskets, diaphragms, and closures. Industrial aprons, gloves, and protective equipment as well as rainproof clothing, tents, and shower curtains are produced by coating fabrics. Calendered and cast sheets and films that are heat-sealing and resistant to moisture are widely used. Special tapes and even shoe soles are also made by these processes.

A series of copolymers with polyvinylidene chloride is also marketed. Those with a high percentage of polyvinyl chloride resemble it in properties, although many properties are modified owing to the presence of the copolymer. Products containing a high percentage of polyvinylidene chloride are discussed under that particular resin.

Both the straight polyvinyl chlorides and the copolymer are available in stable colloidal dispersions resembling a rubber latex. These latices are easily coagulated by alcohol, acids, or polyvalent electrolytes, but in themselves afford a useful coating agent. No organic solvent or oil is required so that simple coating, drying, and baking processes can be used.

In contrast to practice in the United States, unplasticized polyvinyl chloride was used extensively in Germany during the Second World War as extruded sheets, rods, and tubes for chemical-process equipment as a substitute for stainless steel. It was welded with a hot-air torch in the fabrication of valves, tanks, and tubing of large diameter. It was also extensively used in bristles for brushes and brooms. In another German development, the resin was mixed with a cold plasticizer in which it was insoluble and the product was used in the form of a paste. Upon heating, the resin became soluble in the plasticizer, producing thick rubbery sections that were used for everything from rubber sheeting to shoe soles. Other German processing methods were nearly identical with those in the United States.

Chlorinated polyvinyl chloride was also produced on a large scale in Germany. The manufacturing process consisted of dissolving polyvinyl chloride in hot tetrachloroethane, chlorinating the solution, precipitating the resin with methyl alcohol, filtering, washing, and drying. Various grades were produced with chlorine contents varying from 63 to 68 per cent. Most of the production went into the formation of yarns, fabrics, and films. The most important change in properties was an increased solubility in acetone, making it easier to spin, and a higher softening point.

VINYL CHLORIDE-ACETATE COPOLYMERS

Polyvinyl chloride is odorless, difficultly thermoplastic, chemically inert, and nonflammable except when held in direct contact with flame. It is relatively insoluble in all cold solvents, although readily soluble in hot chlorinated hydrocarbons, such as ethylene dichloride or monochlorobenzene. The high softening temperature of this resin makes milling and molding difficult because inadequate heat stability prevents the use of temperatures high enough to relieve strains.

Polyvinyl acetate differs considerably from polyvinyl chloride. It softens at about 40°C. and has outstanding light and heat stability and relatively high water absorbtion. Because of its low softening temperature and sticky nature, the resin is not suitable for milling or molding. Polyvinyl acetate is soluble in alcohols, ketones, esters, chlorinated and aromatic hydrocarbons and insoluble in aliphatic hydrocarbons and water.

From this brief review of the properties of these two substances, it can be seen that polyvinyl chloride has the disadvantage of a very high softening point; polyvinyl acetate, on the other hand, has the disadvantages of softening at too low a temperature and being too easily soluble. These disadvantages offset one another, and each has some properties that any good resin should possess. These facts led to the conclusion that an intimate mixture of the two polymers might combine the attractive properties of both and at least modify their disadvantages. However, when the resulting mixtures were carefully tested, they were found to be too weak and brittle to justify further study. Since even the most thorough mechanical mixing of these polymers failed to effect the desired improvement in quality, it was felt that a simultaneous polymerization of vinyl chloride and vinyl acetate might form a resin that would have attractive properties. Experiments carried out in this direction showed this assumption to be true, and a series of copolymers resulted. New properties were obtained that combined the hardness, water resistance, high softening temperature, nonflammability, and chemical inertness of polyvinyl chloride with the strength, flexibility, and the stability of polyvinyl acetate.

The copolymer resins have excellent strength and resistance to water, acids, alkalies, alcohol, and oil and good electrical insulating properties. Heat stability below 150°F. is good, although continued exposure to elevated temperatures causes an appreciable darkening in color. For this reason, various types of stabilizers are used, including calcium stearate, lead stearate, or white lead.

The properties and applications of the finished product depend on the molecular weight and the vinyl chloride content (see Fig. 89). The lowest molecular weight resins are used in the surface-coatings field. They have a molecular weight of 8,500 to 9,500 and contain 85 to 87 per cent vinyl

chloride. Although this molecular weight is high enough to produce good films, it is still within the range that permits adequate solubility. Solvents are ordinarily ketones that yield solutions of minimum viscosity, supplemented by aromatic hydrocarbons. Surface coatings made from these copolymer resins must be baked at relatively high temperatures in order to secure proper adherence. These lacquers have found extensive use in lining cans, in coating aluminum foil, concrete, asbestos board, and labels, among others.

For injection molding a resin is required that flows readily at the molding temperature and shrinks very slightly in the mold. The copolymer that proved to be most suitable for this purpose has a molecular weight of 9,500
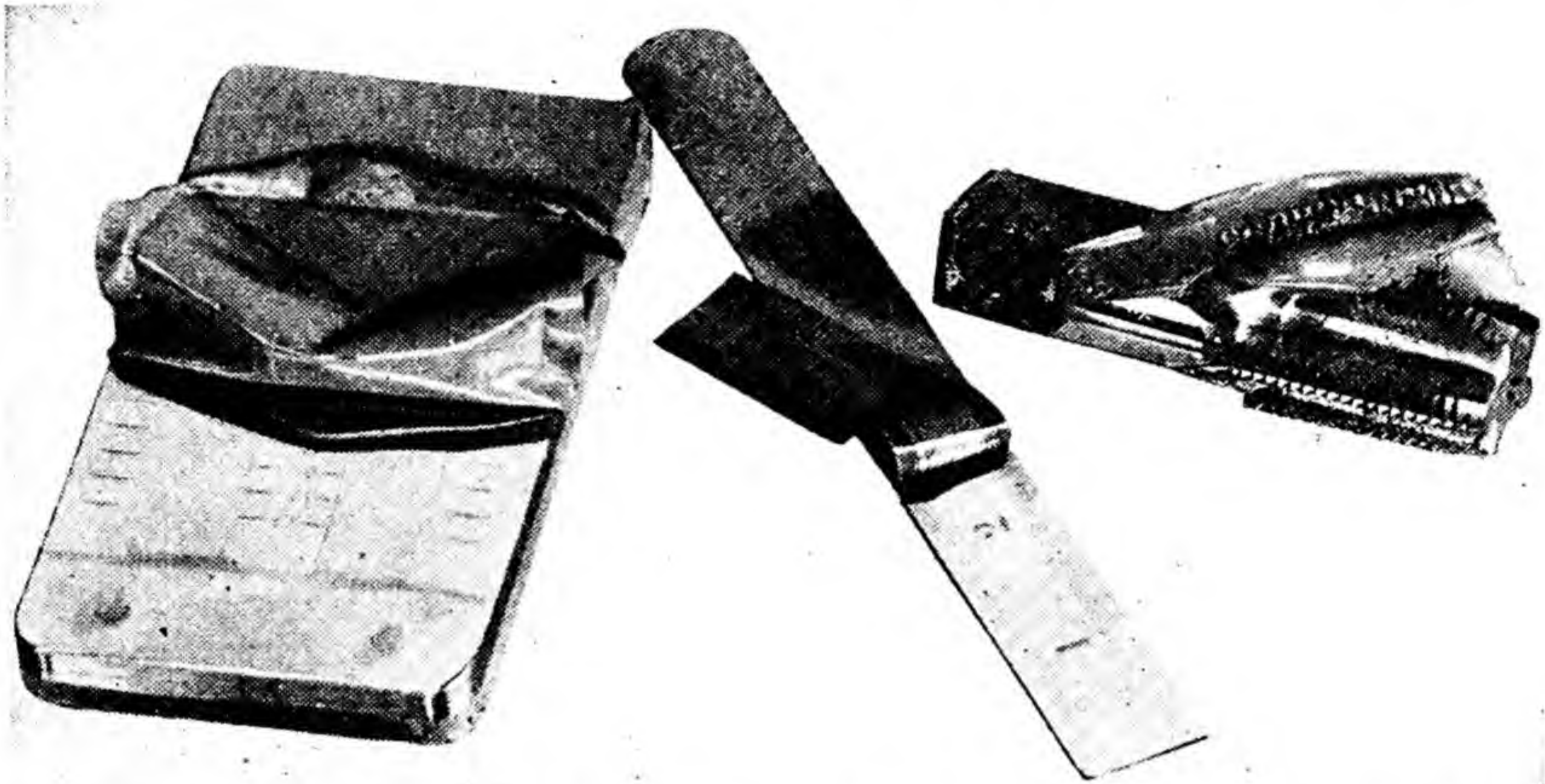
FIG. 89.—Vinyl strip coatings for the protection of machined parts. (*Bakelite Corp.*)

to 10,500 and a vinyl chloride content of 85 to 90 per cent. This resin provides maximum strength and toughness in the molded article and adequate fluidity at the molding temperature. A similar resin is used for coating paper.

For conventional compression molding, a material having an average molecular weight of 12,000 to 13,000 and containing 85 to 88 per cent vinyl chloride is generally used. It is somewhat stiffer at the molding temperature than lower molecular weight resins.

The molded products are thermoplastic with relatively low softening points of about 150°F. They have a wide color range and high dimensional stability. Polyvinyl chloride-acetate resins shrink very little during processing, permitting relatively large moldings to be made and accuracy of reproduction for such items as scales and phonograph records (see Fig. 90). Fillers used are wood flour, mica, talc, and alpha cellulose. In general, the fillers reduce the mechanical strength of the resin and cause a

decrease in water resistance.   Dibutyl phthalate or tricresyl phosphate are used as plasticizers to give a softer, more flexible resin.   The copolymers resemble the cellulose derivatives in their molding characteristics, mechanical strength, and appearance.

In the manufacture of plastic sheets, strength and toughness are required, but it is not necessary that the resin have as high plasticity at molding temperatures as is required in injection molding.   For this purpose a copolymer having a higher average molecular weight (15,000 to
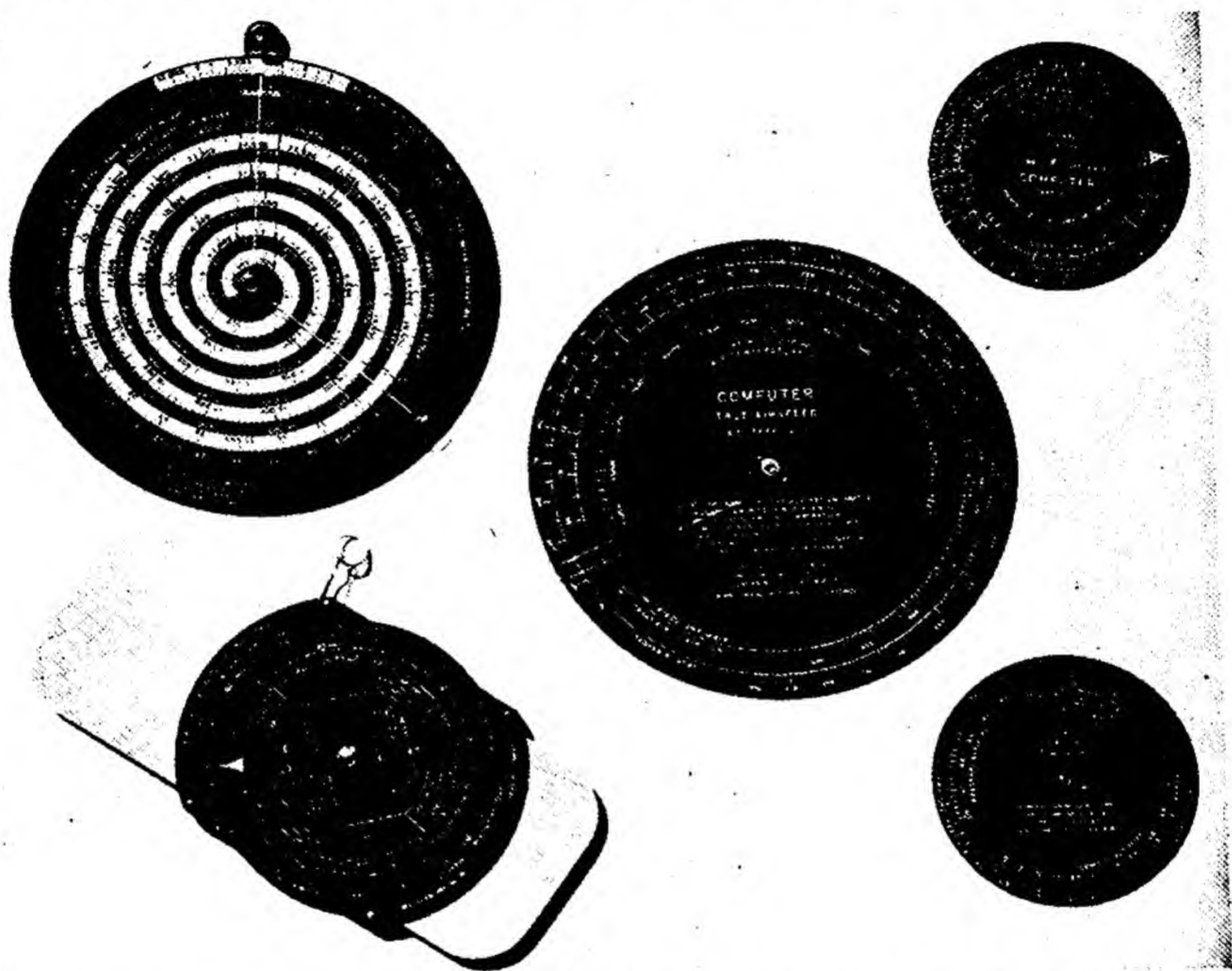
FIG. 90.—Instruments made from vinyl chloride-acetate copolymer and painted with luminous paint.   (*Bakelite Corp.*)

16,000) and containing 88 to 90 per cent vinyl chloride is used.   The strength and water resistance of this resin have made possible the production of a tough, nonclouding, nonwarping sheet that is used for radio dials, instruments, advertising novelties, etc.   These sheets usually contain, in addition to the resin, a suitable plasticizer, pigment, and heat stabilizer. Fillers may be used but are ordinarily unnecessary and tend to lower the mechanical strength and increase water absorption.

A copolymer having a molecular weight of 20,000 to 22,000 and containing 95 per cent vinyl chloride and 5 per cent vinyl acetate may be plasticized on the roll mill with any one of a large number of plasticizers to form a rubberlike mass particularly suitable for coated wire and tubing.   Coated

wire is usually fabricated by extruding the plasticized resin around the wire. The desired hardness is obtained by adjusting the concentration of plasticizer. Electrical properties are good, and chemical inertness is much superior to that of rubber.

These copolymers are also used to produce a synthetic fiber. Two types have been developed, one having a molecular weight of 16,000 to 19,000 and the other a molecular weight of 20,000 to 23,000, both resins containing 88 to 90 per cent vinyl chloride. The fiber is made by extrusion from solution through spinnerettes, solvent being removed by warm air. The resin is used at the rayon plant in the form of a white powder of very fine consistency. It is first dissolved in acetone in mixers and then filtered and stored in tanks. In the dissolving process, it is kept at a temperature of about 50°C. At the time of being stored in the tanks, the heated solution is clear and has the general appearance of a heavy sirup. In this state it is known as "dope." The dope is then pumped to the spinning machine, which is standard acetate-spinning equipment. The process here is substantially the same as that used in making acetate rayon, except that higher air pressures and temperatures are used. As with acetate, the dope is converted to a textile yarn at the spinning machine. These yarns must be stretched to increase tensile strength and reduce extensibilities, oiled, twisted, and redrawn on spools or cones.

The tenacity may be controlled at will within the range of 1.0 to 4.0 g. per denier and the elongation within the range of 120 to 180 per cent, an increase in tenacity producing a reduction in elongation. The yarn is definitely and permanently water-resistant. Surface wetting may be accomplished by the use of wetting agents. Temperatures in excess of 65°C. will cause shrinkage of the yarn, the shrinkage varying with temperature.

Vinyon synthetic textile yarns and fabrics are exceptionally resistant to mineral acids and alkalies. At room temperature the fabric is not attacked by 70 per cent nitric acid, aqua regia, hydrochloric or hydrofluoric acids of maximum concentration, 30 per cent sodium hydroxide, or 28 per cent ammonium hydroxide. It is likewise resistant to salt solutions, etc. It is dissolved by ketones and is softened or partly dissolved by esters, certain halogenated hydrocarbons, ethers, certain amines, and lower aromatic hydrocarbons. It is unaffected by alcohols, glycols, and aliphatic hydrocarbons.

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PROPERTIES AND USES

OF

POLYVINYL ACETATE AND CHLORIDE

</div>

Advantages:
    Very high flexural strength
    Good tensile strength
    Little tendency to cold flow
    Good acid and caustic resistance

Low water absorption
Good solvent resistance
Fair electrical properties

Disadvantages:
Low softening point (150°F.)
Adverse effect of sunlight (slight)
Instability toward heat (polyvinylchloride)

Common uses:
Polyvinyl acetate
Adhesives
Inks
Plastic woods
Putty

Polyvinyl chloride'
Cable coverings
Coated fabrics
Extruded tubes
Tank linings
Tubing
Gaskets

Copolymer
Belts and supenders
Films
Floor tile
Sound records
Watch straps
Vinyon
Coatings
Tubing

POLYVINYLIDENE CHLORIDE

Monomeric vinylidene chloride, 1, 1-dichloroethylene, is a colorless liquid boiling at 31.7°C. In the carefully purified state it polymerizes very slowly but can be readily polymerized with the aid of peroxide catalysts into long-chain polymers.

$$CH_2{=}CCl_2 \longrightarrow \left[-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}- \right]_n$$
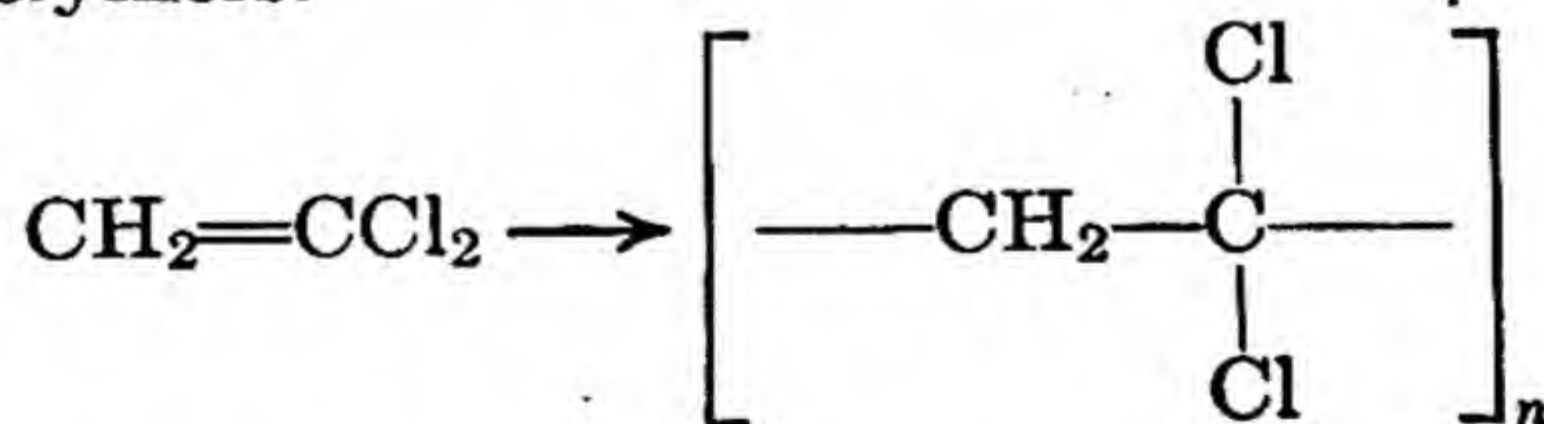
Polyvinylidene chloride is a white porous powder with a softening range of 185 to 200°C. and a decomposition temperature of about 225°C. Polyvinylidene chloride possesses two outstanding characteristics: crystallinity, as determined by X-ray diagrams, and insolubility. Variations of polymerization and copolymerization with vinyl chloride result in a group of related resins with varying properties. It is possible to obtain materials

ranging from the soft and flexible with a softening point around 70°C. to hard, rigid, and tough polymers with a softening point of about 180°C. The standard polymer is a thermoplastic solid with a softening point of approximately 120 to 140°C., having a molecular weight of about 20,000 (see Fig. 91).

The high softening point and relative thermal instability of polyvinylidene chloride have largely excluded it from the industrial-fabrication procedures for which the copolymers of lower softening temperatures are more adaptable. The copolymers now available require special techniques in
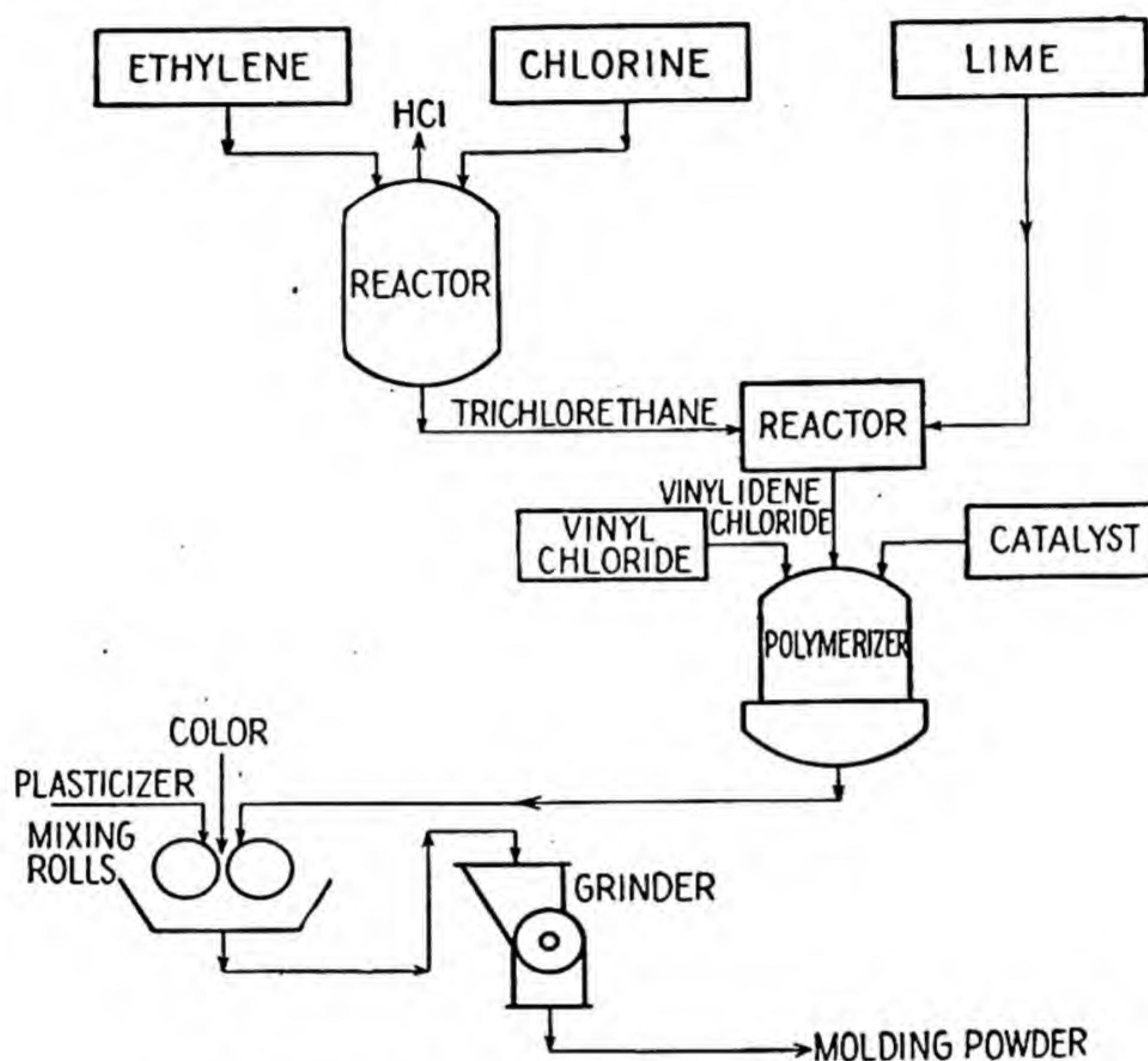
Fig. 91.—Flow sheet for polyvinylidene chloride.

their fabrication. Important considerations are the use of inert metals in hot zones, minimum heating times, and the incorporation of a satisfactory plasticizer and heat stabilizer.[1]

Injection moldings of vinylidene chloride copolymers possess unusual toughness and durability. The use of cold dies results in supercooled articles suitable for further treatment, while heated dies permit crystallization, which is desirable for rapid cycles and dimensional accuracy of the finished piece. Economic considerations usually favor injection molding.

X-ray diffraction studies of polyvinylidene chloride show well-defined rings indicating a high degree of crystallinity, while background scattering indicates an appreciable amount of amorphous polymer, which can be crystallized at elevated temperatures. Stretching of either completely

[1] REINHARDT, R. C., *Ind. Eng. Chem.*, **35**, 422 (1943).

amorphous or partly crystalline polymers produces orientation. According to Reinhardt,[1] polyvinylidene chloride and copolymers that are largely vinylidene chloride exist in three modifications:

1. *Crystalline.* The normal "as-polymerized" state, giving a sharply defined X-ray pattern but also known to be partly amorphous.

2. *Amorphous.* Soft, easily deformed material obtained by fusing and rapidly cooling crystalline polymer; reverts to the crystalline form under suitable conditions.

3. *Oriented Crystalline.* Tough and strong, showing characteristic X-ray fiber pattern; produced by plastically deforming either partly crystalline or amorphous material.

Under normal molding conditions the crystals are arranged in a heterogeneous manner, but even in this condition, good properties are obtained. Tensile strength is about 5,000 to 8,000 lb. per sq. in. Extrusion produces continuous shapes of approximately the same strength. By special temperature control and annealing, oriented linear crystals are obtained and the tensile strength of extruded shapes is increased to 20,000 to 40,000 lb. per sq. in. Flexibility and fatigue are also increased by orientation.

The relative insolubility and unreactivity of polyvinylidene chloride is not greatly altered by copolymerization with vinyl chloride until the copolymer contains less than about 85 per cent vinylidene chloride; consequently, the commercially available copolymers are resistant to the action of all but a few common materials. At temperatures above 100°C., compounds of the type of dioxane, ortho-dichlorobenzene, and cyclohexanone show some solvent action. At room temperature, high vinylidene chloride copolymers are substantially unaffected by both aliphatic and aromatic hydrocarbons, alcohols, esters, and ketones. Inorganic acids and alkalies have little or no effect, with the exception of concentrated sulfuric acid, sodium hydroxide, and ammonium hydroxide, which cause discoloration. Resistance to water is exceptional.

Polyvinylidene chloride is extruded into monofilaments and tapes that are oriented by heat-treatment to produce unusually strong abrasion-resistant materials. These materials are woven into upholstery for buses and trains and outdoor furniture. Their resistance to weathering and moisture gives extreme durability, and their chemical and moisture resistance permits easy cleaning with relatively strong cleaning agents. These same properties indicate that recently developed window and insect screening may be far more satisfactory than metal screening, while the flexibility of this material permits the mounting of the screen on rolls similar to window shades.

Special tubing and pipe are extruded in large quantities. The tubing is

[1] *Ibid.*

particularly useful and economical. At low temperatures, it has a wider range of use in contact with chemicals than does copper tubing since it is inert toward most acids, bases, and salts, even including nitric and hydrofluoric acids. Extruded tubing and pipe are sold under the trade name Saran. Injection-molded flare-type fittings for tubing .and standard fittings for pipe are made of the same material, so that piping layouts are all of one material that has the same thermal expansion and chemical resistance. The pipe can be threaded with ordinary dies and is easily welded by forcing together ends that have been heated to the softening point.

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PROPERTIES AND USES

OF

POLYVINYLIDENE CHLORIDE PLASTIC
</div>

Advantages:

    Exceptional chemical resistance
    Good solvent resistance
    Good electrical properties
    Low moisture absorption
    Good aging properties
    Availability in a wide range of colors
    High strength

Disadvantages:

    Poor thermal stability
    Low thermal conductivity
    Adverse effect of sunlight ("fogs" slightly)
    Relatively low maximum permissible temperature (160 to 200°F.)

Common uses:

    Leaders for fish lines
    Screens to replace metal-woven screens
    Railway and streetcar seat covers and chair seats
    Tubing and fittings

POLYSTYRENE

This resin is a polymer of styrene (vinyl benzene), $C_6H_5CH{=}CH_2$. Large-scale commercial production was started in the United States in 1937, although it had been in production in Germany for some years. Prior to this time, several concerns were making it on a laboratory scale, chiefly for test purposes. It has many very desirable properties, but many of its possible commercial applications depended on cheaper styrene. The tre-

$$CH{=}CH_2 \longrightarrow \left[-CH{-}CH_2- \right]_n$$
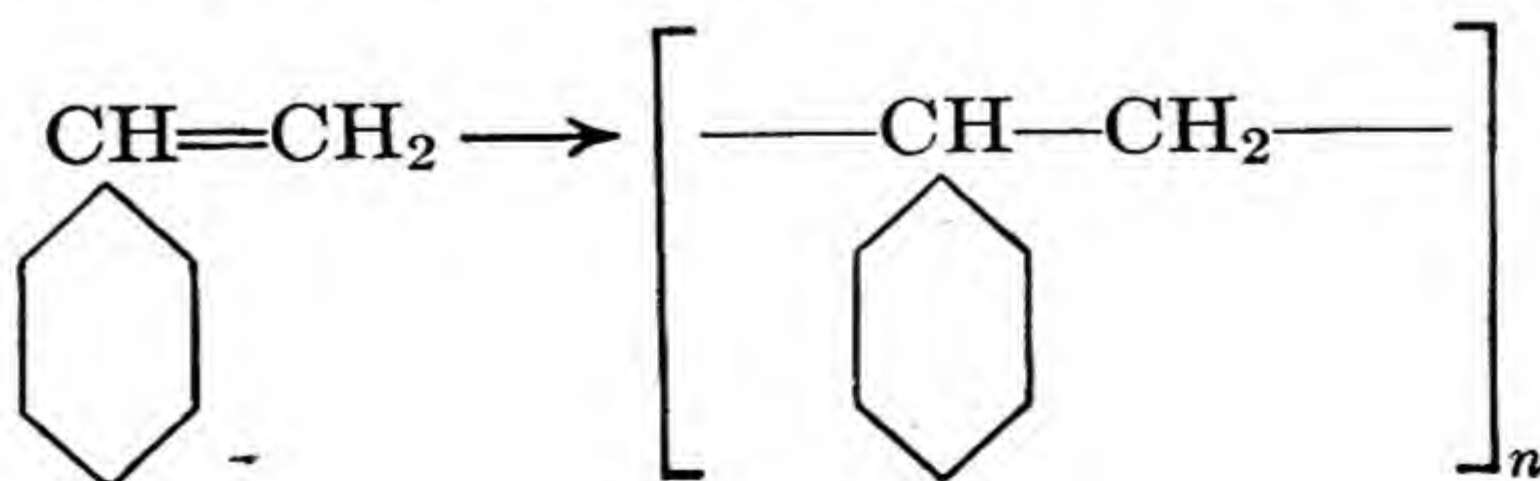
mendous synthetic-rubber development during the war period caused styrene to be produced on a scale that was undreamed of before.   There is a
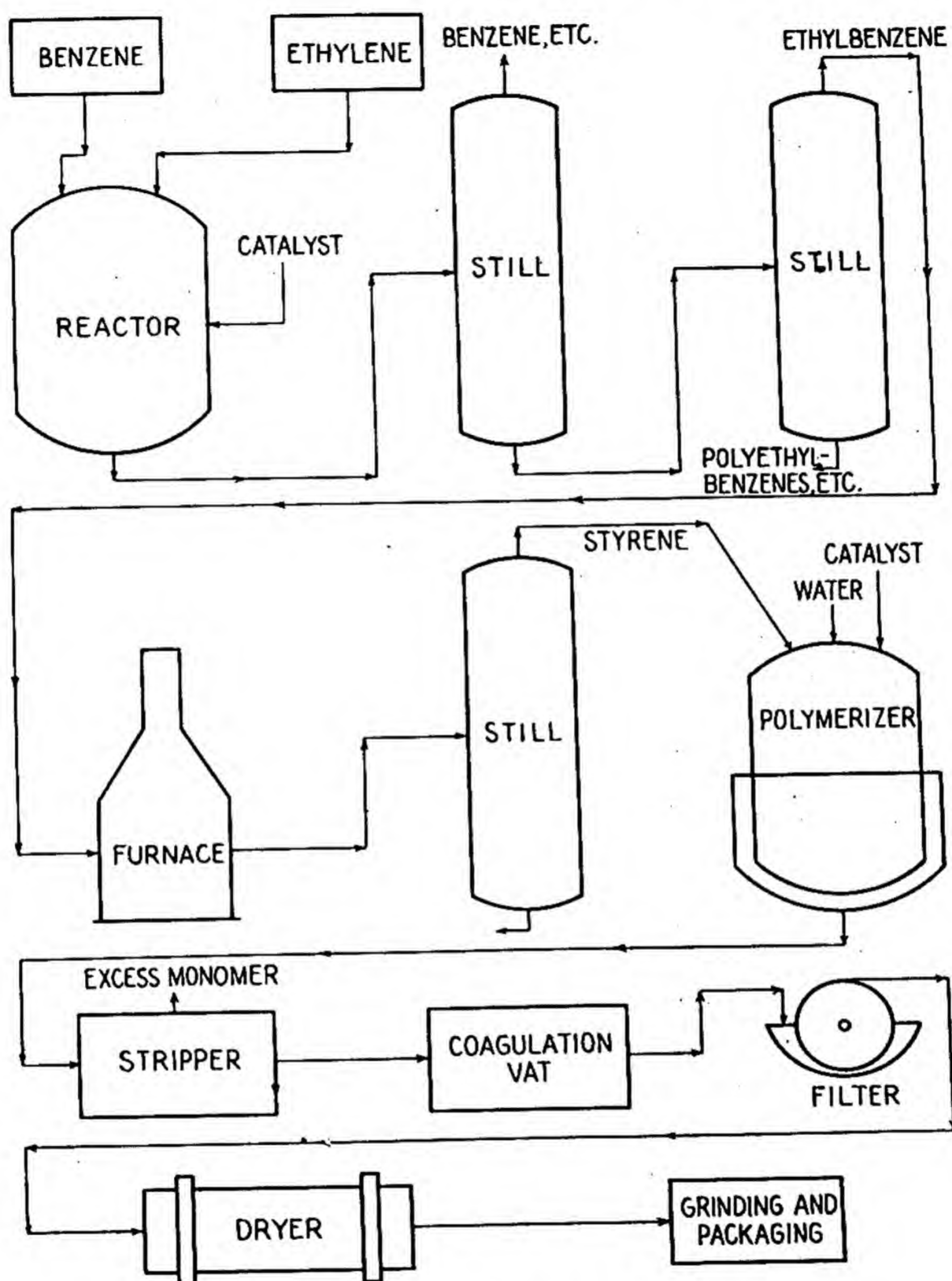
FIG. 92.—Flow sheet for polystyrene.

possibility that a portion of this tremendous capacity may produce relatively cheap styrene when and if the demand for synthetic rubber decreases.

Polystyrene is a typical thermoplastic chain polymer. The monomer will polymerize very slowly at room temperature to form polymers of high molecular weight. At elevated temperatures it will polymerize readily, but the degree of polymerization decreases as the temperature increases.

The polymerization is catalyzed by peroxides as are the other resins of this class. Emulsion polymerization methods are employed to produce a wide range of molecular weights (see Fig. 92). A continuous mass polymerization process was developed in Germany in which the monomer was prepolymerized to about 33 per cent and the resulting viscous liquid was continuously polymerized by permitting it to flow slowly downward through heated towers. The finished product was extruded in the form of a tape from the base of the tower. A similar process employed heated rolls for the final polymerization, scraping off the finished product in the form of flakes.

Polystyrene has been investigated as completely as any other plastic, at least from a theoretical standpoint. Staudinger developed his macromolecular theory chiefly from investigations on the formation and properties of polystyrene. He carefully prepared polystyrene of different degrees of polymerization and showed that the viscosity of solutions of this material is a function of the length of the linear chain. He has also illustrated the dependence of other properties on the chain length. Work on this material has supplied proof of the theory that thermoplastic and thermosetting resins are caused by linear and three-dimensional structures. If even small amounts of divinyl benzene are added to styrene before polymerization, the resulting polymer becomes insoluble and has a very much higher softening temperature. The incorporation of divinyl benzene permits occasional cross linkages between the linear chains to give a partial three-dimensional structure:

$$—\!\!\!—CHCH_2—CHCH_2—CHCH_2—CHCH_2—CHCH_2—\!\!\!—$$

$$—\!\!\!—CHCH_2—CHCH_2—CHCH_2—CHCH_2—CHCH_2—\!\!\!—$$
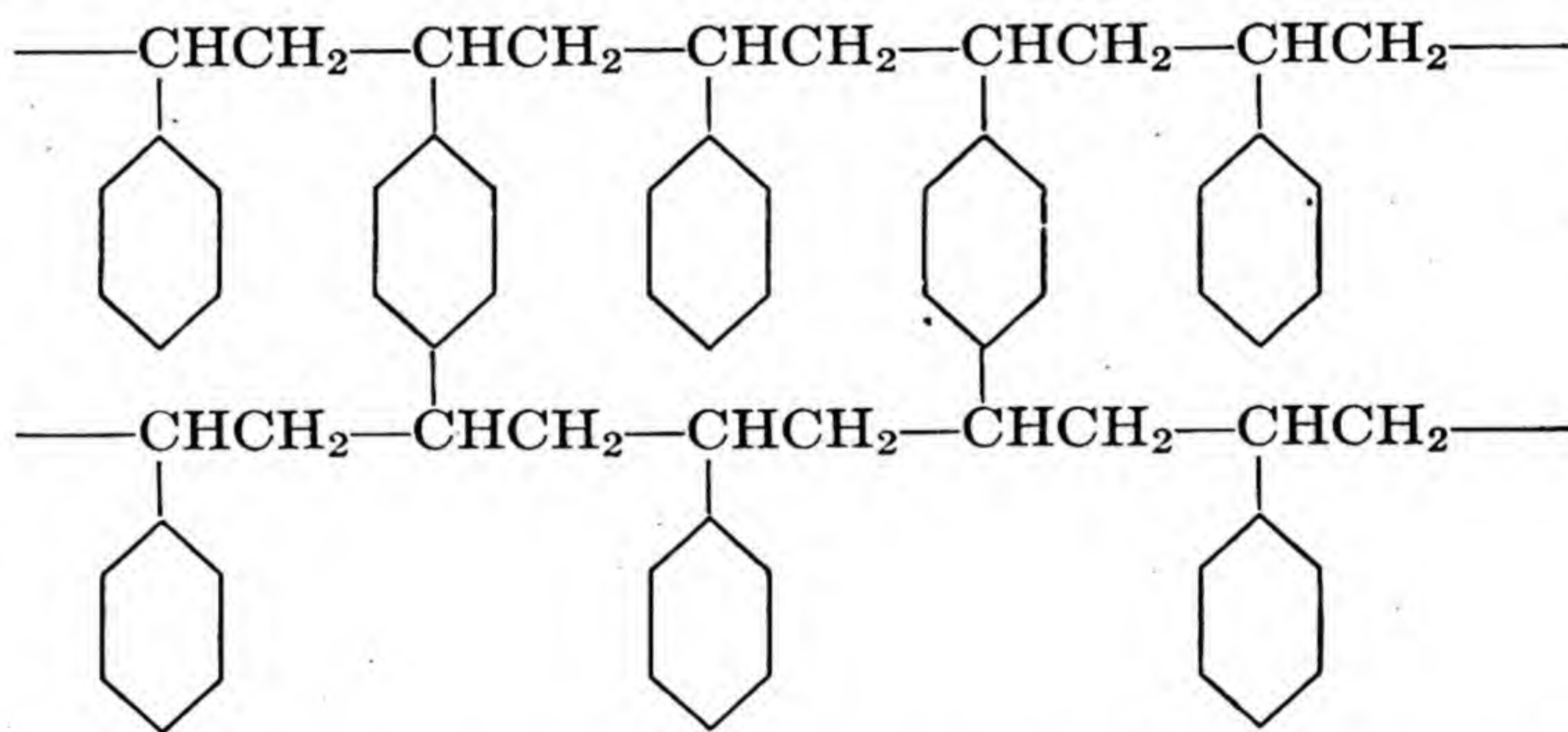
Polystyrene rods that are thermosetting in character are produced by the inclusion of small amounts of divinyl benzene. These materials have exceptionally high heat distortion and are used in the electrical industry for special insulators. They have also been g ound and polished for certain optical applications.

Polystyrene does not tend to form crystallites even in the stretched state. This behavior is attributed to the fact that considerable branching of the

chains may occur. Copolymers are formed with many other monomers such as the copolymer with butadiene, which is the most important of the synthetic rubbers.

Molded polystyrene is used in the chemical industry for bottle closures, adapters, bottles, and special ware. It is used for closures on mineral acid bottles because it is resistant to high acid concentrations (see Fig. 93). Each type of acid can be quickly identified by the color of the closure. The closures eliminate contamination and make the task of opening the bottle much easier. Another improvement in chemical laboratory equipment is the acid bottle adapter and the acid siphon and pump that are
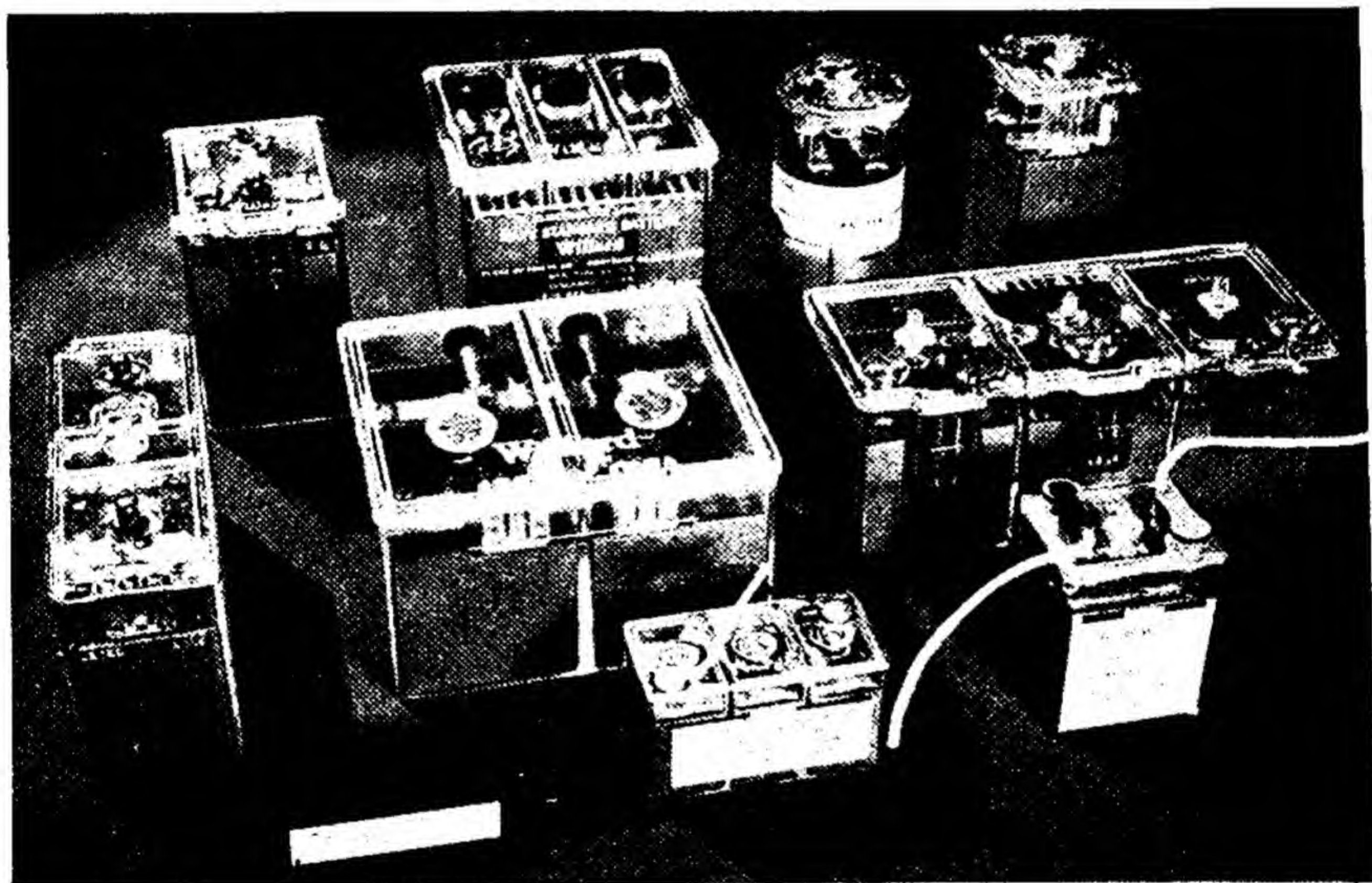
FIG. 93.—Battery boxes made from polystyrene. (*The Dow Chemical Co.*)

designed to fit the screw-type acid bottles. They not only make the pouring of acids a simple matter, but also eliminate the possibility of acid burns from spilling and careless handling. Bottles for acids and a wide range of other chemicals are blown into molds in a process very similar to the blowing of glass. The bottles are unbreakable and will handle hydrofluoric and nitric acids as well as strong bases.

One of the unique properties of polystrene is that it is capable of transmitting light through curved sections. Thus a light at one end of a curving rod or sheet will be transmitted out of the other end. This characteristic is employed in the illumination of aircraft instruments, providing adequate illumination of the instrument without blinding the pilot during night flying. Because of this ability to transmit light around corners, the material is used for illuminated signs, automotive instrument

panels, radio and television receiver panels, etc. Letters and numerals can be molded directly into the piece and the panel lighted from the edge, providing a very novel effect as the numerals and letters glow and seem to stand out with exceptional clarity.

Radio and television make use of considerable quantities of polystyrene because of its excellent electrical properties. It has a low dielectric constant and a very low power factor, which make it ideally suited for coil
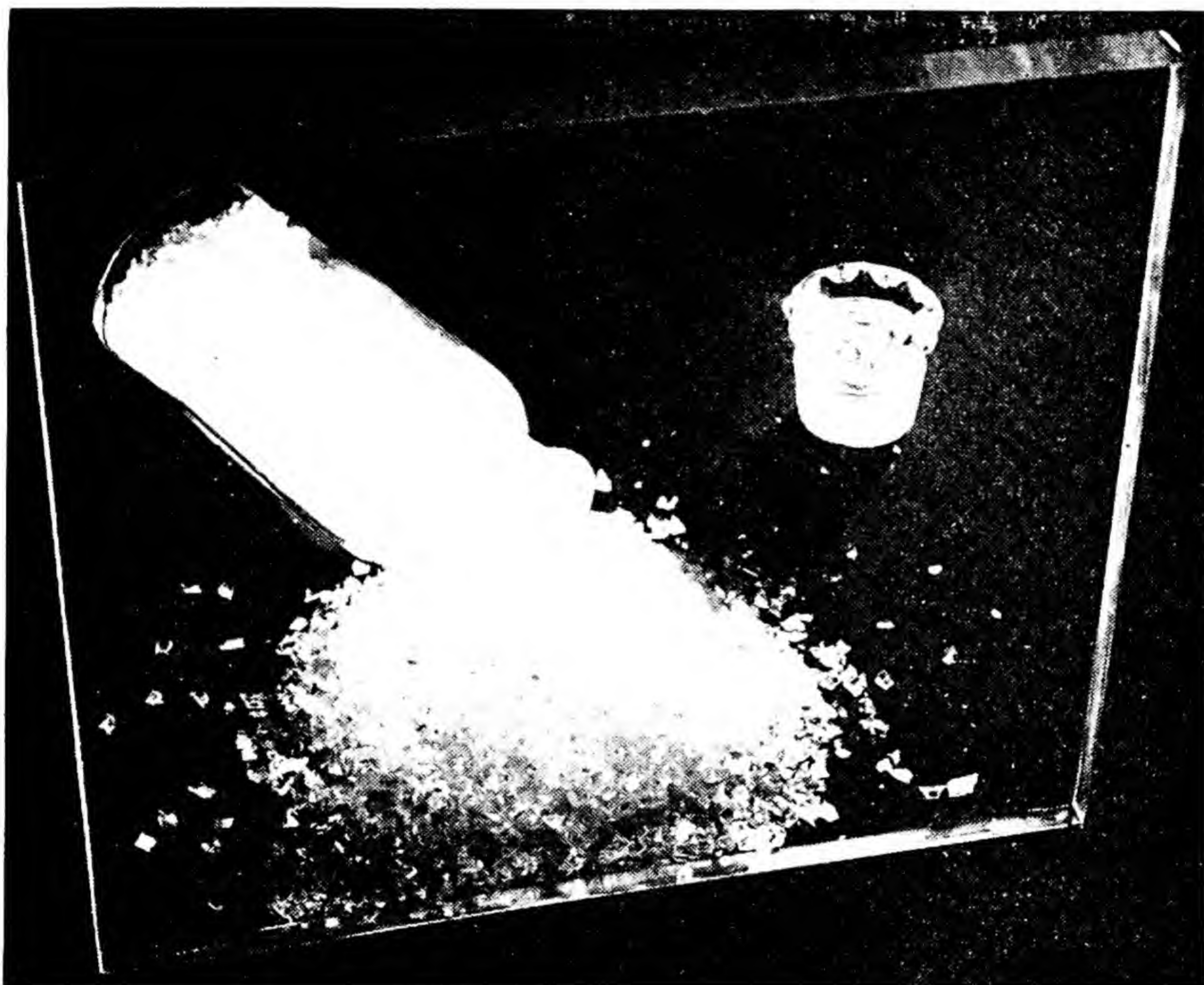
FIG. 94.—Photograph showing the high clarity of polystyrene sheets. (*The Dow Chemical Co.*)

forms, lead bushings, and condensers, particularly for high frequencies where these properties become extremely important.

Styrene is now cast into sheets (see Fig. 94) by pouring the liquid monomer into the space between two glass plates, carefully eliminating air, and then causing polymerization to take place over a long period of time in an oven having close temperature control. Sheets are available varying in thickness from $\frac{1}{8}$ up to 2 in. and as large as 36 by 38 in. They are clear, with polished surfaces, and show no signs of strain.

Small amounts of polystyrene have appeared on the market as fibers, but its use for this purpose is still in the development stage.

Specially plasticized and compounded polystyrene has been produced

that has rubberlike qualities as well as being inert. In this respect it has many of the properties of polyvinyl chloride. For use as a rubbery material, however, the chlorostyrenes seem to have many definite advantages.

Polydichlorostyrene.—Although polystyrene possesses excellent electrical properties and is one of the most inert resins, its low softening point, in the neighborhood of 200°F. or less, precludes its use wherever high heat resistance is required. Polymerized dichlorostyrenes have much better heat resistance and are even more inert than polystyrene. Although all the various dichlorostyrene isomers polymerize readily, the 2,5 dichlorostyrene is used.
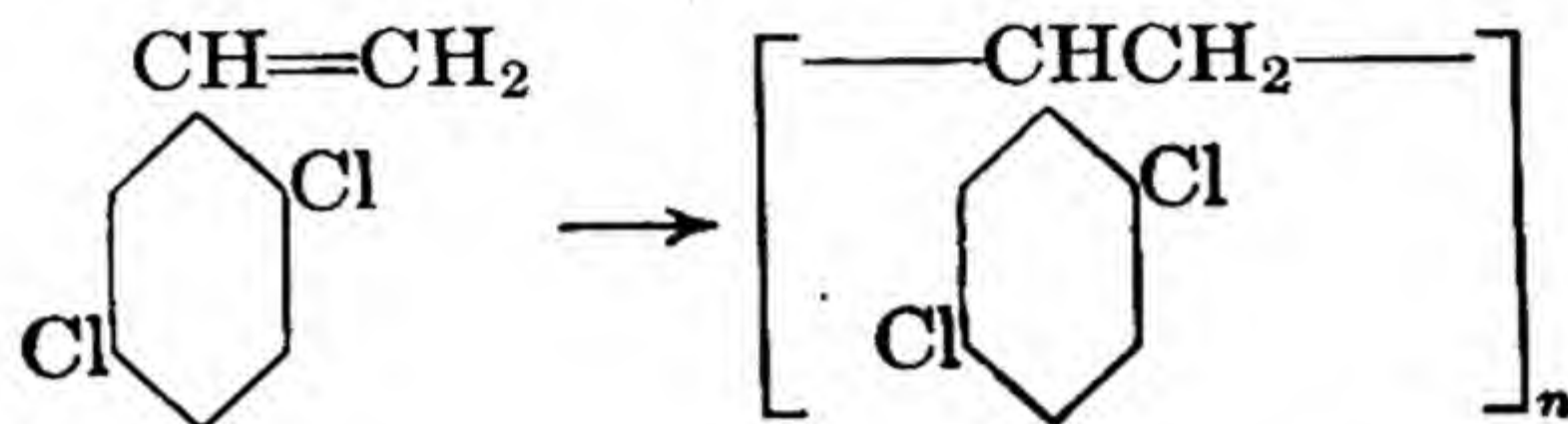
High purity of the monomer and careful control of the polymerization reaction is required to produce a heat-resistant product.

The polymer has a distortion temperature of 240 to 265°F.,[1] is self-extinguishing, has high tensile strength, and is more compatible with plasticizers than is polystyrene. Water absorption is low, and polydichlorostyrene is unaffected by hydrochloric, nitric, and sulfuric acids as well as all common alkalies at room temperature. It is soluble in aromatic hydrocarbons, chlorinated compounds, ketones, and some esters and ethers.

Dichlorostyrene copolymerizes readily with other vinyl compounds, dienes, and other materials, having conjugated double bonds. When copolymerized with butadiene, it produces a rubber that is superior to the ordinary GR-S synthetic rubber.

In spite of its many advantages, the higher cost of the monomer will limit its use to applications that require a material of superior quality.

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PROPERTIES AND USES

OF

POLYSTYRENE PLASTIC

</div>

Advantages:

> Low specific gravity
> Excellent electrical properties
> Very low water absorption
> Excellent resistance to acids and alkalies
> Nontracking characteristic
> Excellent molding properties
> Fair tensile strength
> Fair resistance to impact
> Availability in all colors

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[1] MICHALEH, J. C., and C. C. CLARK, *Chem. Eng. News*, **22**, 1559 (1944).

Disadvantages:

Slight dimensional change with age
Low softening point (190°F.)
Tendency to craze
Poor light stability

Common uses:

Airplane instrument panels
Combs and novelties
Containers for acids and alkalies
High-frequency radio and television parts
Costume jewelry and ornaments
Lenses
Closures

ACRYLIC POLYMERS

Acrylic resins are prepared from the esters of acrylic acid and the methyl derivative, α-methyl acrylic acid.

$$CH_2\!\!=\!\!CHCOOCH_3 \longrightarrow \left[\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{CH}\!-\!\right]_n$$

$$CH_2\!\!=\!\!C(CH_3)COOCH_3 \longrightarrow \left[\!-\!CH_2\!-\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!-\!\right]_n$$
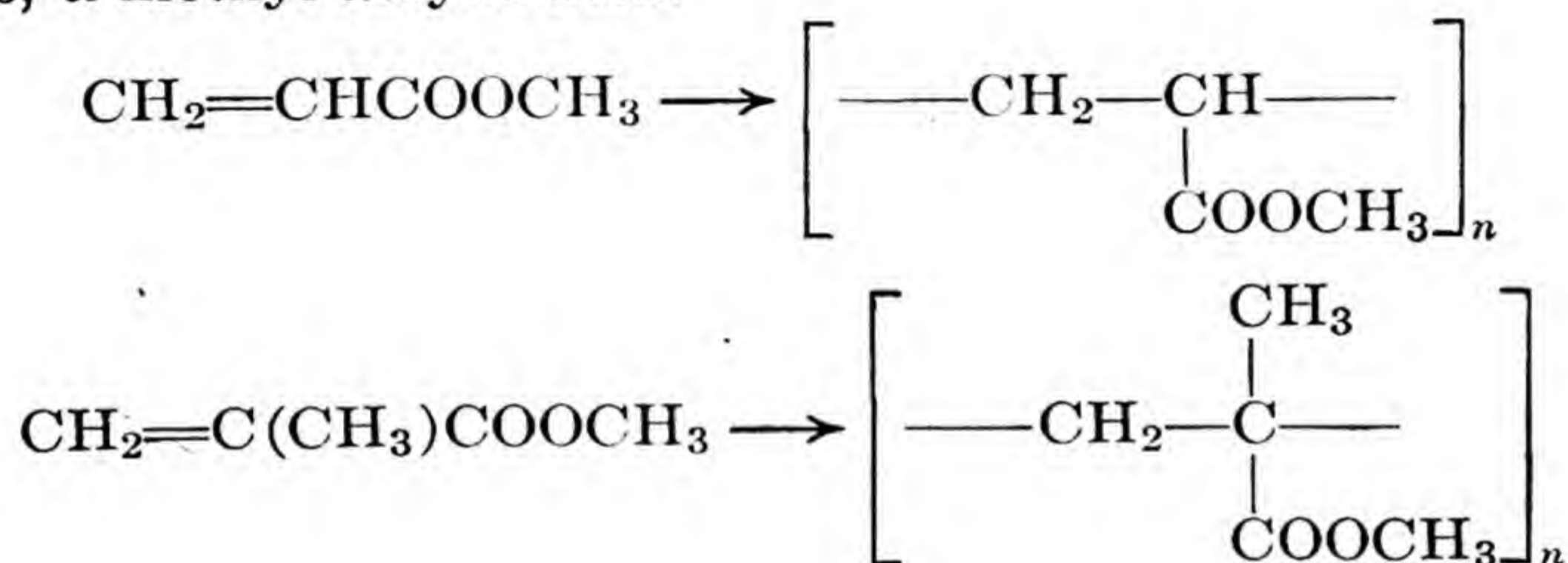
These esters polymerize readily at their boiling points or at lower temperatures in the presence of catalysts of the oxygen-yielding type such as benzoyl peroxide or ammonium persulfate. The emulsion method of polymerization is used for the production of molding powders. An aqueous dispersion medium is first prepared containing an emulsifier, which is usually a soap, a stabilizer, and the catalyst. The acrylic ester is then dispersed in this aqueous phase. The polymerization produces a suspension that is easily coagulated with salt, or with salt and acid, filtered, washed, and dried to give a granular or powdered product (see Fig. 95).

The various acrylic resins range from soft, sticky, semiliquids to hard, tough, thermoplastic solids. With the softer members of the series, plasticizers are not used. The hardest products are the methyl esters. As the ester alkyl group increases in molecular weight from methyl through ethyl, propyl, and butyl, the esters progressively become softer and more nearly liquids at the same degree of polymerization.

At the present time, the greatest percentage of production is in the form of cast sheets of polymethyl methacrylate. In this process, either the monomer itself or a viscous liquid prepared by the careful mass polymerization of the monomer to a low degree of polymerization is poured

into a narrow container whose sides are made of glass plates. The liquid contains a polymerization catalyst. The glass containers are put into polymerization ovens where they are gently heated for several days. Provision must be made for shrinkage. After special heat-treatment, the
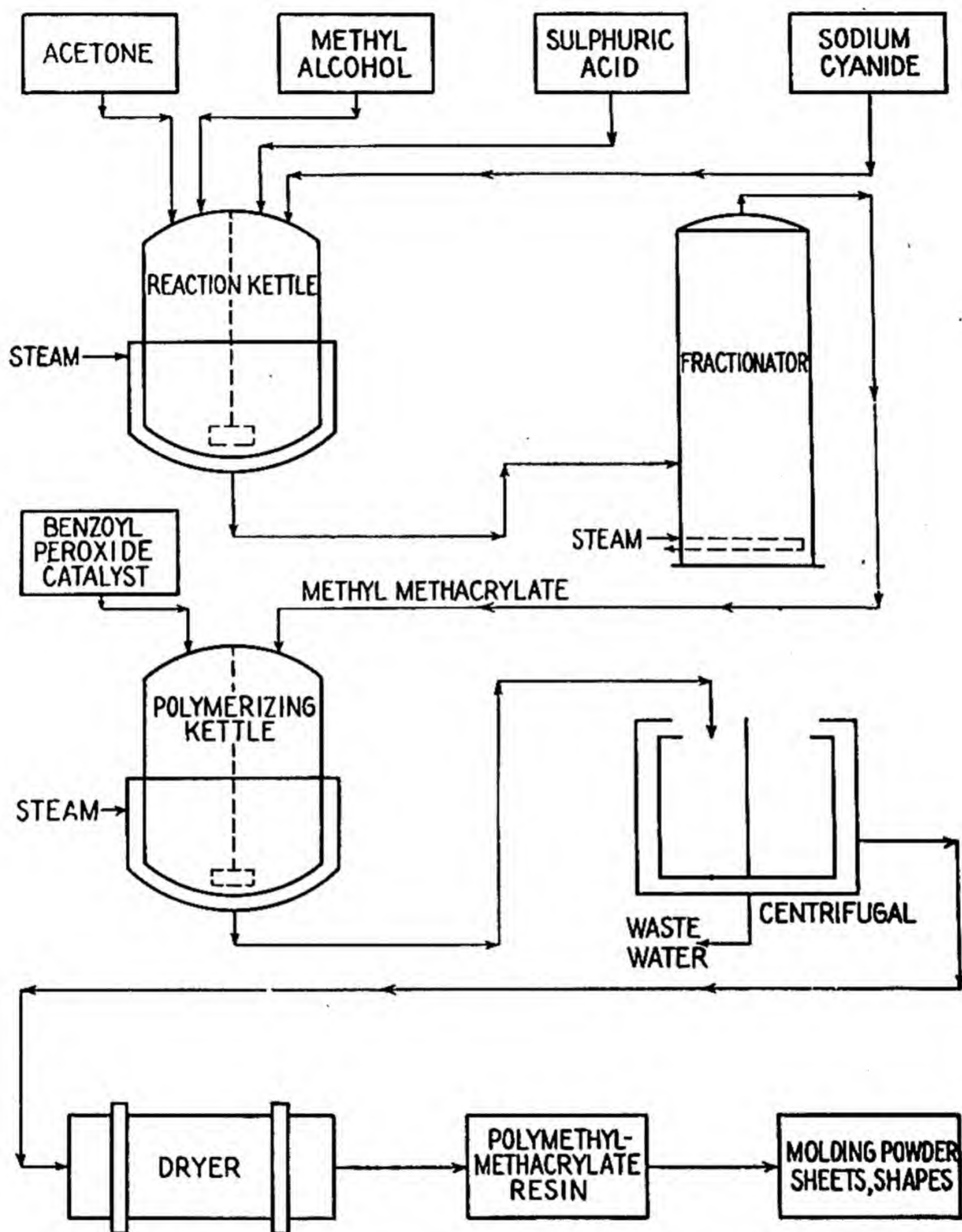
FIG. 95.—Flow sheet for polymethyl methacrylate.

glass plates are removed to yield clear sheets up to 36 by 48 in. in area and ¼ to ⅜ in. in thickness. Sheets up to 2 in. in thickness are prepared by modifications of this casting process. Cylinders and rods are also made by casting (see Fig. 96).

The plastic is crystal clear, light in weight, tough and durable, and flexible in thin sections. It may be cut, turned, sawed, drilled, polished,

swaged, or formed. It takes lacquers and pyroxylin stains of the proper type; is not affected by alkalies, oils, dilute acids, or dilute alcohols; and is resistant to moisture and the harmful effects of sun and outdoor exposure. It has the property of transmitting light; a rod will transmit light around bends.

The high clarity and excellent light transmission of polymethyl methacrylate, coupled with its resistance to sunlight and its low density, make this
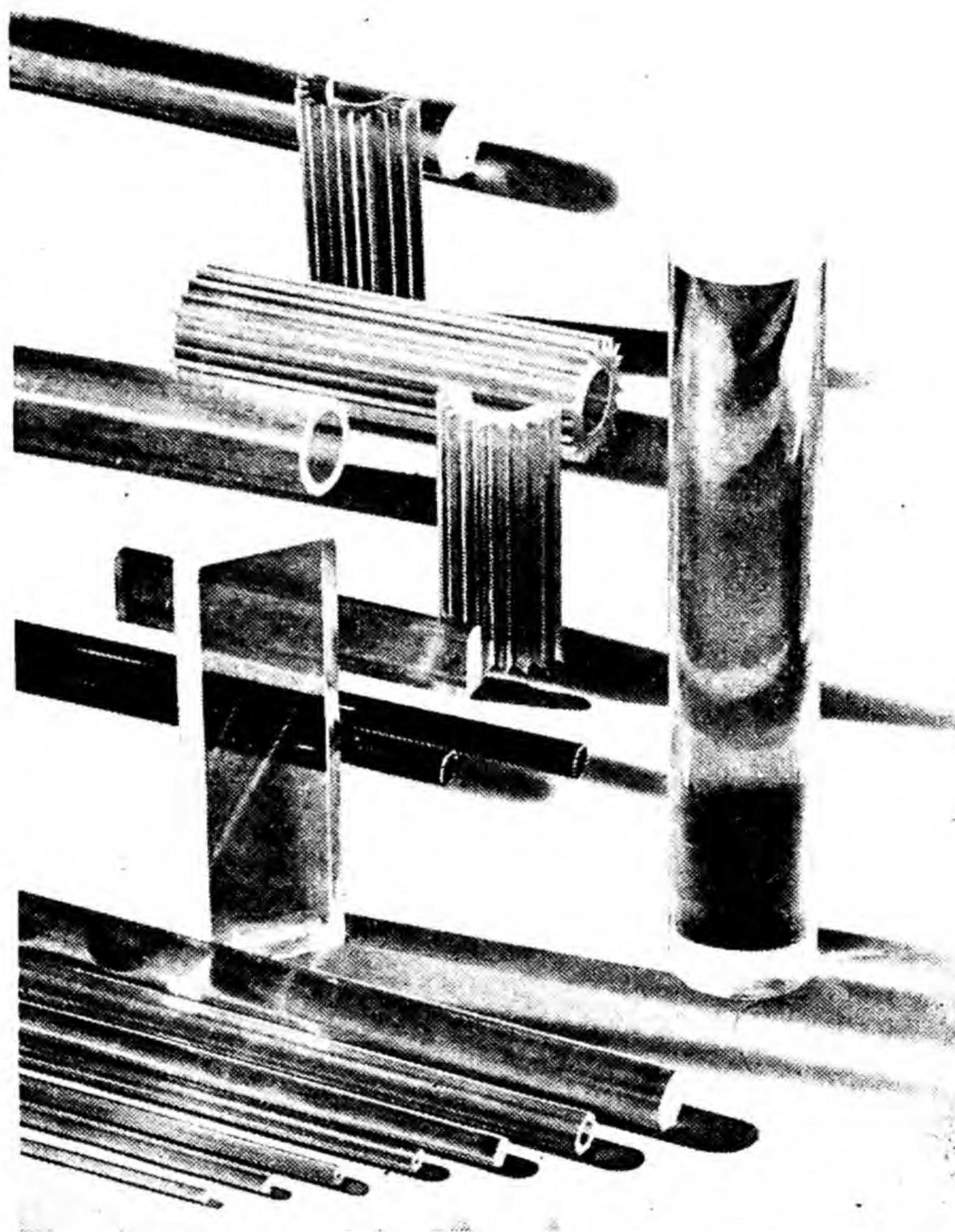
FIG. 96.—Standard rods and tubes of polymethyl methacrylate. (Courtesy of Bruce Lindsay and Plax Corp.)

resin ideally suited to production of airplane windows, cockpit closures, bomber noses, and the like. Cast sheets are formed by blowing, by the use of vacuum, molding, and by a great variety of special forms and jigs. A high degree of optical accuracy is maintained even in curved sections so that gun and bomb sighting can be done accurately.

The greatest defect of polymethacrylate sheets as a substitute for glass is the much lower degree of scratch hardness. When used as airplane windshields and blisters, frequent polishing is necessary and deep scratches are impractical to remove.

The cast acrylates soften at temperatures of 190 to 240°F. Moldings will withstand temperatures of 140 to 190°F., depending on the grade of molding powder used. A special heat-resistant variety will withstand even higher temperatures for short periods.

These resins are soluble in ketone and ester solvents as well as aromatic hydrocarbon–alcohol mixtures. Their water resistance is good so that they are unaffected by solutions of most salts. Dilute alkalies and hydrochloric and sulfuric acids do not affect them.

Acrylic polymers are outstanding in their high clarity and index of refraction. In addition, they have excellent machining properties and are easily molded. They form good adhesives so that plastic parts may be cemented without leaving a noticeable joint. They are easily colored with the use of special dyes. These properties, together with the ability to transmit light around corners, make them desirable for the production of decorative and ornamental objects of all types. These same properties have been responsible for the use of the various shapes in the building of transparent models of machine units and parts. Whole model plants have been constructed.

PROPERTIES AND USES OF ACRYLIC RESINS

Advantages:

    High transparency and clarity
    Excellent light transmission
    Good flexural strength
    Relatively good weathering and aging properties
    Availability in all colors

Disadvantages:

    Tendency toward cold flow
    Low softening point (140 to 220°F.)
    Moderate chemical resistance
    Low scratch resistance

Common uses:

    Airplane windshields and cockpit covers
    Dental plates
    Fillers and stiffeners for fabrics
    Costume jewelry
    Roadside-sign reflectors
    Safety goggles
    Window displays

POLYVINYL ETHERS

The polyvinyl ethers are a recent addition to the class of polyethenic resins. In Germany during the war their development was accelerated by a shortage of polyacrylates, to which they bear a close resemblance in physical properties and uses.

The production of the monomer vinyl ethers was a result of the classic

work of Reppe,[1] who found that aliphatic alcohols or phenols will react with acetylene in the presence of an alkali metal.

$$ROH + HC\equiv CH \longrightarrow CH_2\!=\!CH\!-\!OR$$

The methyl, ethyl, and isobutyl vinyl ethers have had the greatest use commercially. Polymerization is carried out massively, using boron trifluoride as a catalyst (see Fig. 97). Copolymers have been made of the methyl or ethyl vinyl ethers with decalol vinyl ether.

All the polyvinyl ethers are somewhat soft and find use in adhesives and lacquers. as well as for impregnation of paper and textiles.
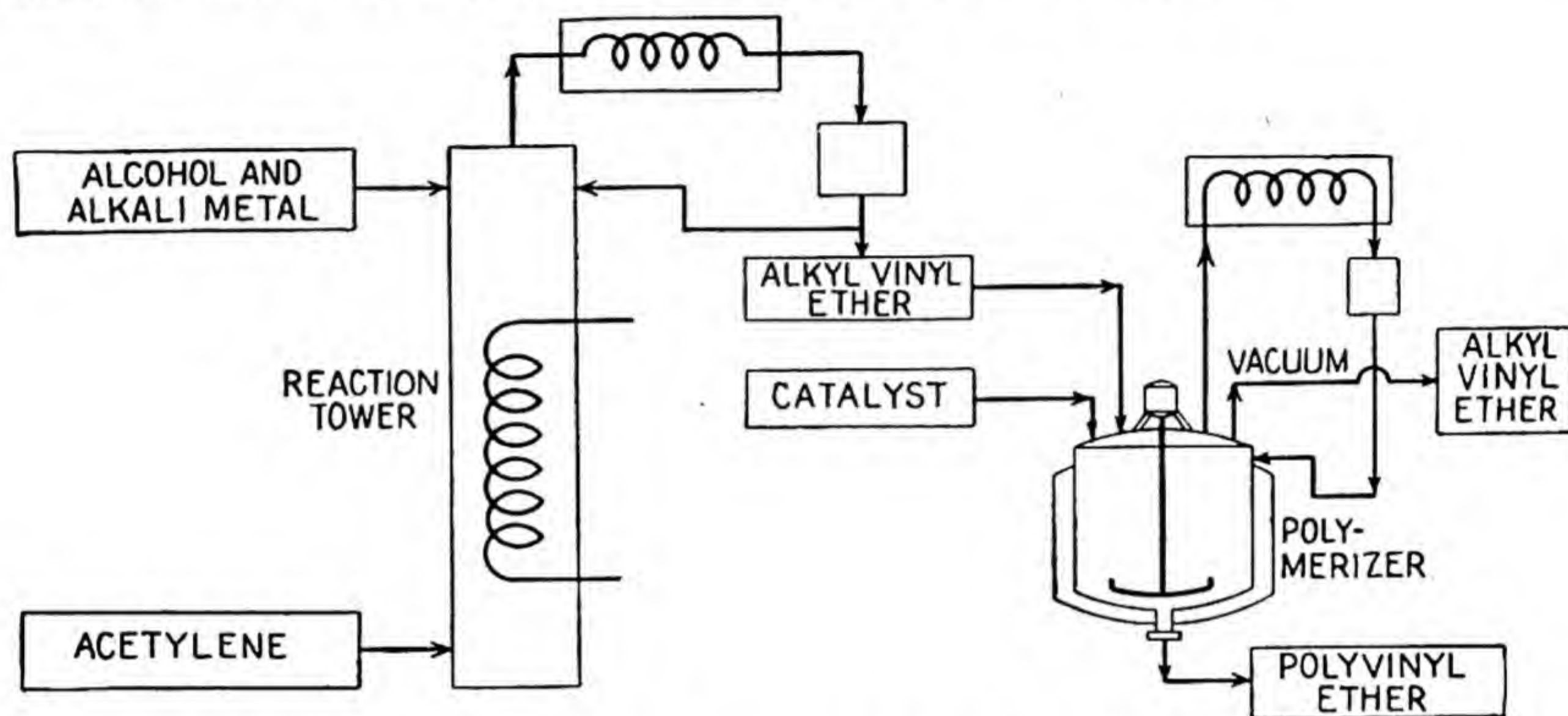
FIG. 97.—Flow sheet for polyvinyl ethers.

POLYVINYL KETONES

The polyvinyl ketones are a class that have not been commercially exploited in this country. In England, there has been some small-scale production.

One reason for the lack of progress in commercial development of these resins is that no clean-cut and economical method has been worked out for the synthesis of the pure monomers.

The methyl vinyl ketone can be prepared by reacting acetone with formaldehyde to form the methylol compound with the subsequent splitting out of water.

$$CH_3\!-\!CO\!-\!CH_3 + CH_2O \longrightarrow CH_2OH\!-\!CH_2\!-\!CO\!-\!CH_3$$
$$CH_2OH\!-\!CH_2\!-\!CO\!-\!CH_3 \longrightarrow CH_2\!=\!CH\!-\!CO\!-\!CH_3$$
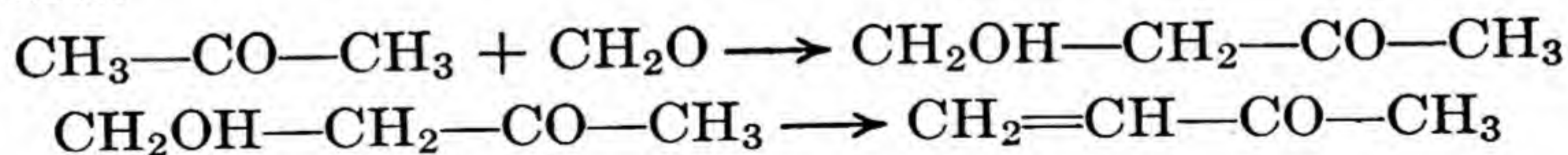
The yield of methyl vinyl ketone is very low and its recovery in the pure state very difficult owing to its tendency to polymerize readily, even in the absence of catalyst. It forms a soft resin resembling polymethyl acrylate.

[1] Office of the Publication Board, Department of Commerce, *Rep.* 4149.

The methyl isopropenyl ketone is formed similarly to the first member of the series, employing methyl ethyl ketone instead of acetone. It polymerizes readily with peroxide catalysts and forms a harder polymer than the methyl vinyl ketone. However, its polymerization is complicated by the simultaneous formation of the dimer, which gives a cloudy and insoluble resin. Methyl isopropenyl ketone forms copolymers with styrene and methyl methacrylate.

POLYVINYL AMINES

The polyvinyl amines constitute a new class of polymeric materials still in the development stage.

Vinyl carbazole can be polymerized to a product of very high melting point which has been called "man-made mica." It is a chain polymer.
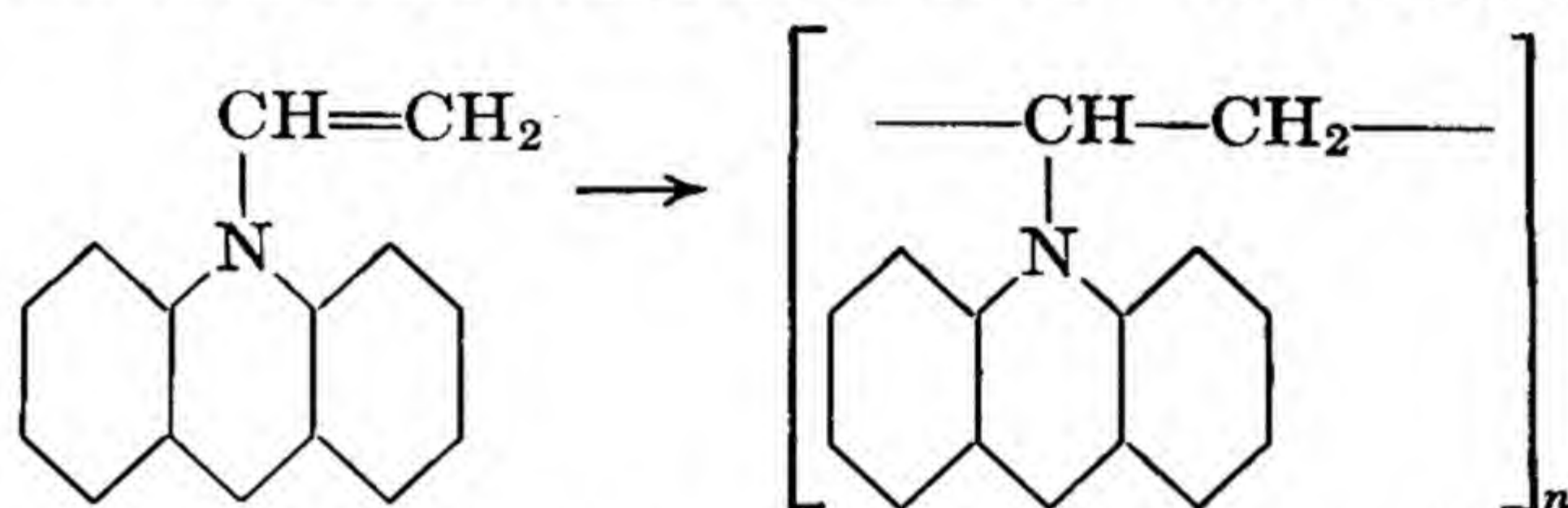
The monomeric vinyl carbazole is made by reacting potassium carbazole in the presence of zinc oxide with acetylene at elevated temperature and pressure. The polymer has low plasticity and can be molded only in flat sheets. Copolymerization with styrene improves its molding properties.

N-vinyl pyrrolidine is made in a similar manner to the vinyl cabazole by reacting acetylene with pyrrolidine. It polymerizes to a water-soluble resin that has been used in dilute water solution as a blood-substitute liquid. It forms a chain polymer of the following structure:
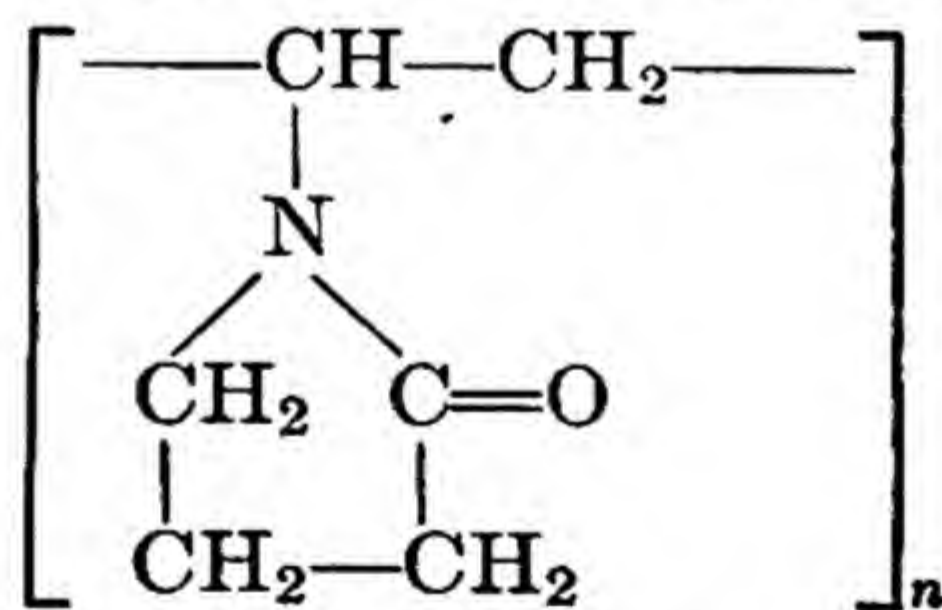
A somewhat different type of polymer is obtained from ethylene imine.
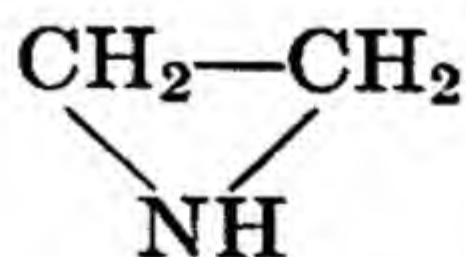
This compound polymerizes by the breaking of one of the nitrogen to carbon bonds, and a linear polymer is formed containing a nitrogen atom in the unit structure of the chain.

$$(-CH_2-CH_2-NH-)_n$$
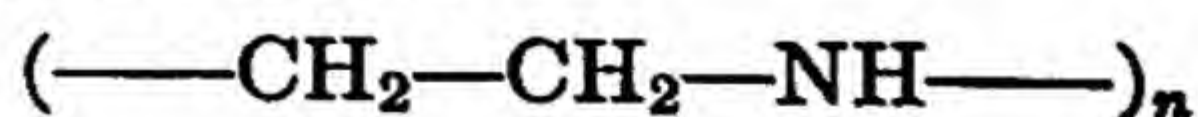
This polymer is likewise water-soluble.

DIVINYL POLYMERS

Divinyl polymers are classified as those produced from monomers containing two vinyl groups that are not conjugated with respect to carbon to carbon double bonds.

The most important members of this series, the allyl resins, are a recent addition to the commercial polymers. Their development depended in part on the availability of allyl alcohol on a tonnage basis, and in part on their unique properties. They form a marked exception to the generalized properties of ethenic resins, although their final cure depends on addition polymerization involving the opening of a double dond. The most important difference is that they are thermosetting rather than thermoplastic. This property is not so unexpected once the method of their polymerization is understood.

Allyl alcohol itself is not polymerized directly, but a special monomer is first formed by esterification or condensation reactions with a dibasic acid or a glycol. If phthalic anhydride is the dibasic acid used, the monomer would be formed as follows:
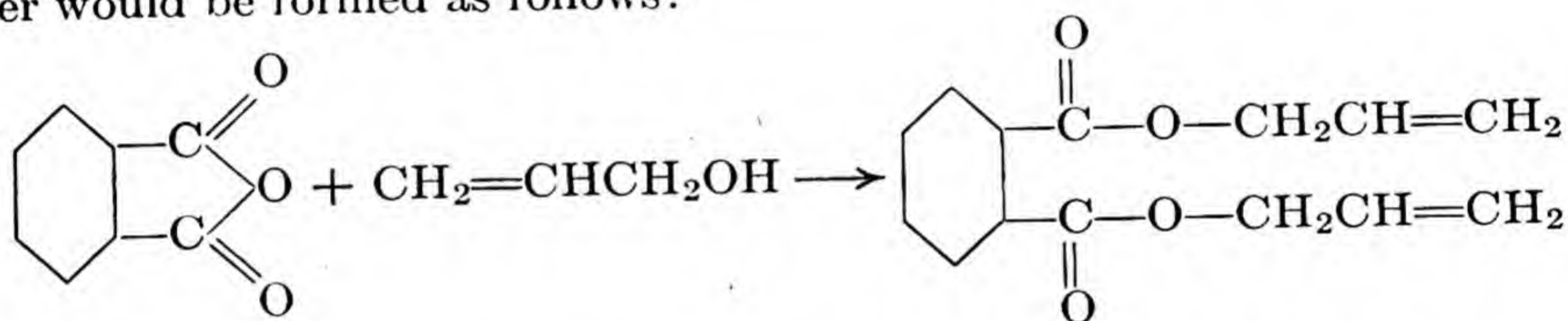
This diester contains two double bonds through which typical addition polymerization can take place. The liquid monomer has a very low volatility and can be heated to over 200°C. before decomposition takes place. It also has a relatively low viscosity. These properties facilitate the handling, storage, and application of the monomer.

Polymerization takes place in the neighborhood of 100°C. in the presence of benzoyl peroxide to catalyze the reaction. Since both double bonds are capable of polymerizing, a complicated three-dimensional structure results in which the recurring unit is
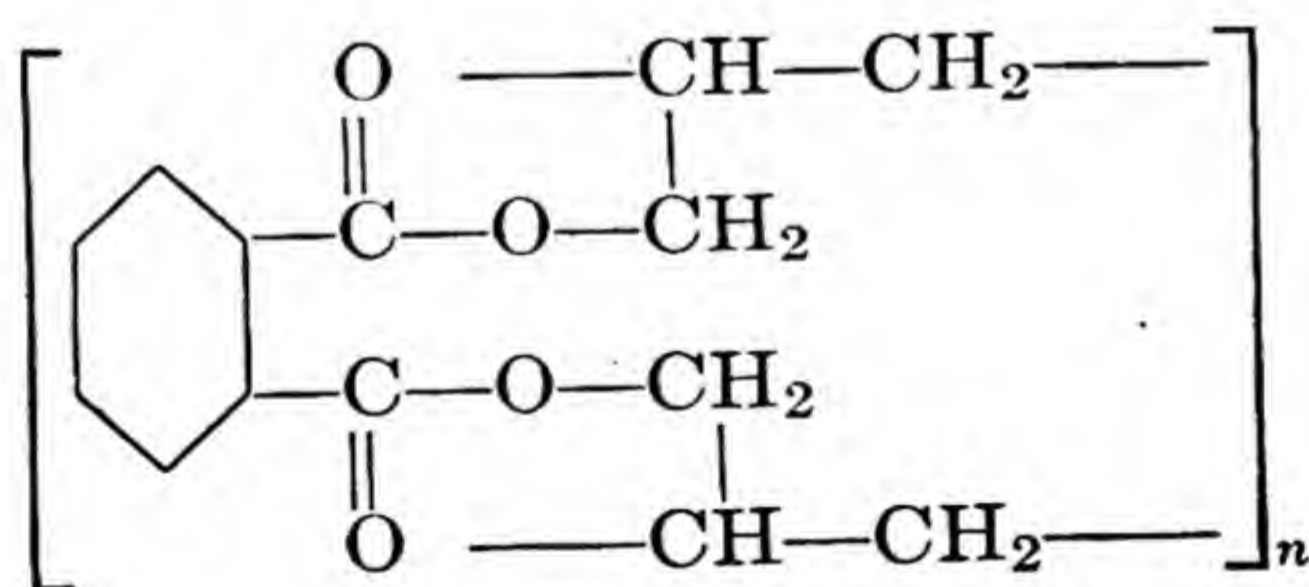
This type of structure offers many possibilities of cross linkage and chain formations.

The final cure takes place without the liberation of water since it is an

addition polymerization and not a condensation. Thus it differs from the thermosetting resins of class II and is one of the reasons pressure is not required for the final cure. It also eliminates the need for venting molds. The fact that pressure is not required for final cure and the ease of application of the monomer without the troubles inherent in the use of a solvent to lower the viscosity make these resins ideally suited to the low-pressure molding technique. Their use in preparing shaped laminates of this type is increasing rapidly, as the products are of high strength and excellent quality.
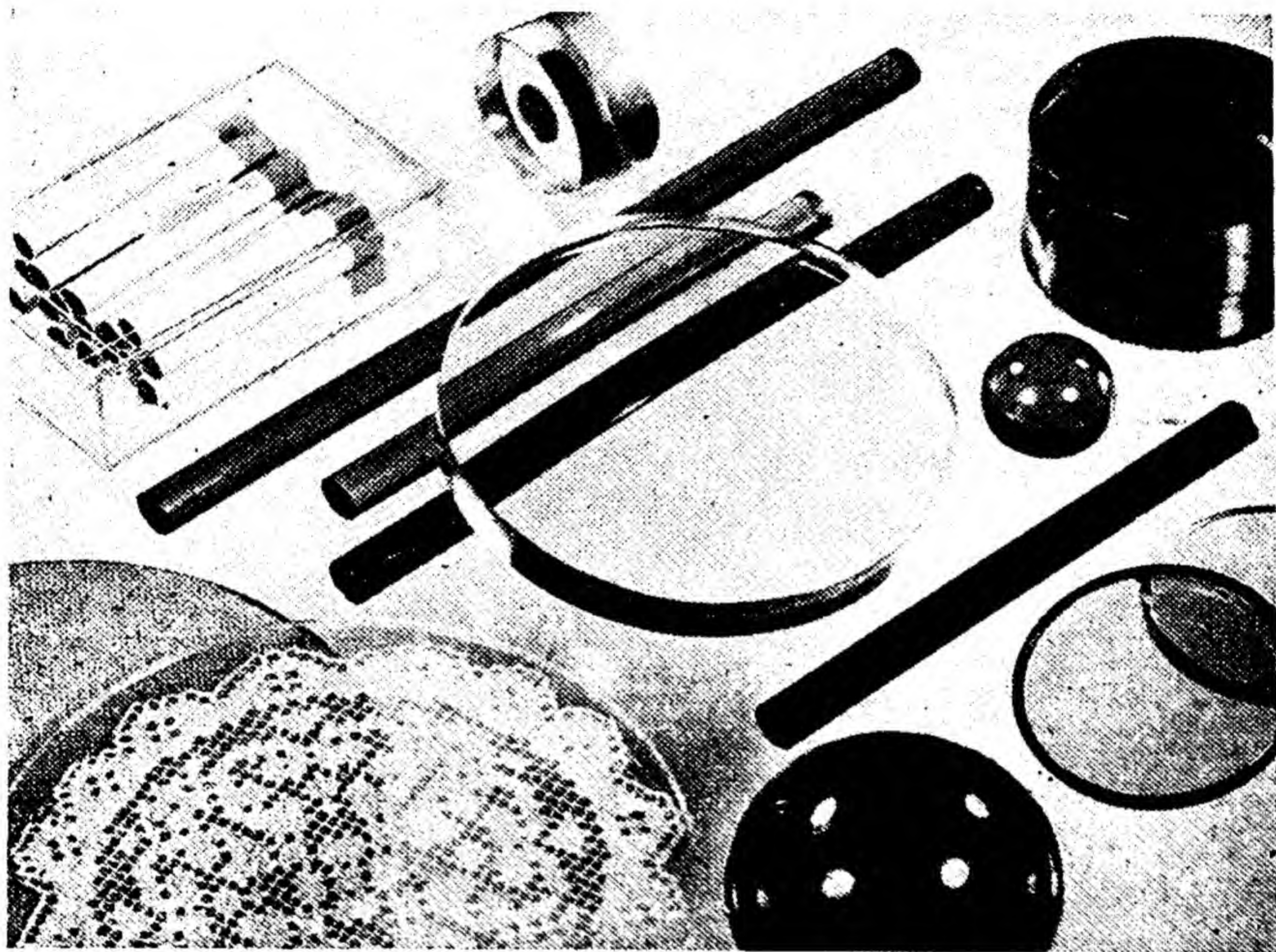
Fig. 98.—Various objects made from divinyl polymers illustrating excellent transparency. (*B. F. Goodrich Co.*)

The resin in the final cured state is still clear and transparent. The refractive index is about the same as polymethyl methacrylate so that it has the same brilliant appearance. Its advantages are due to its thermosetting properties, which give it good heat resistance and a much harder surface. The harder surface promises to make this resin useful for lenses, windowpanes, and closures where glass is not suitable because of weight or the danger of breakage (see Fig. 98). The process of forming sheets, rods, and special forms is similar to the casting process for polymethyl methacrylate.

The products differ, however, from the polymethyl methacrylates in that they soften but slightly at 100°C. and sheets can be bent only on a

rather large radius. They can be heated to comparatively high temperatures without losing rigidity.

The allyl resins possess two distinct disadvantages. The polymerization is inhibited by atmospheric oxygen so that the final cure must be carried out in the absence of air. In the casting process, a marked shrinkage occurs during polymerization, as much as 14 per cent. This requires the use of special molds to accommodate the change in volume.

The vinyl group may be introduced by other means than through allyl alcohol, and monomers are formed that behave similarly. For example, esters can be made from acrylic acid and ethylene glycol or the glycol ethers. The ester from diethylene glycol gives the following unit structure upon polymerization:

$$\left[\begin{array}{l} \qquad\qquad\overset{\displaystyle ---CH-CH_2---}{\underset{\displaystyle CH_2-CH_2-O-C=O}{|}} \\ \overset{\displaystyle O}{|} \\ \overset{\displaystyle CH_2-CH_2-O-C=O}{\underset{\displaystyle ---CH-CH_2---}{|}} \end{array}\right]_n$$
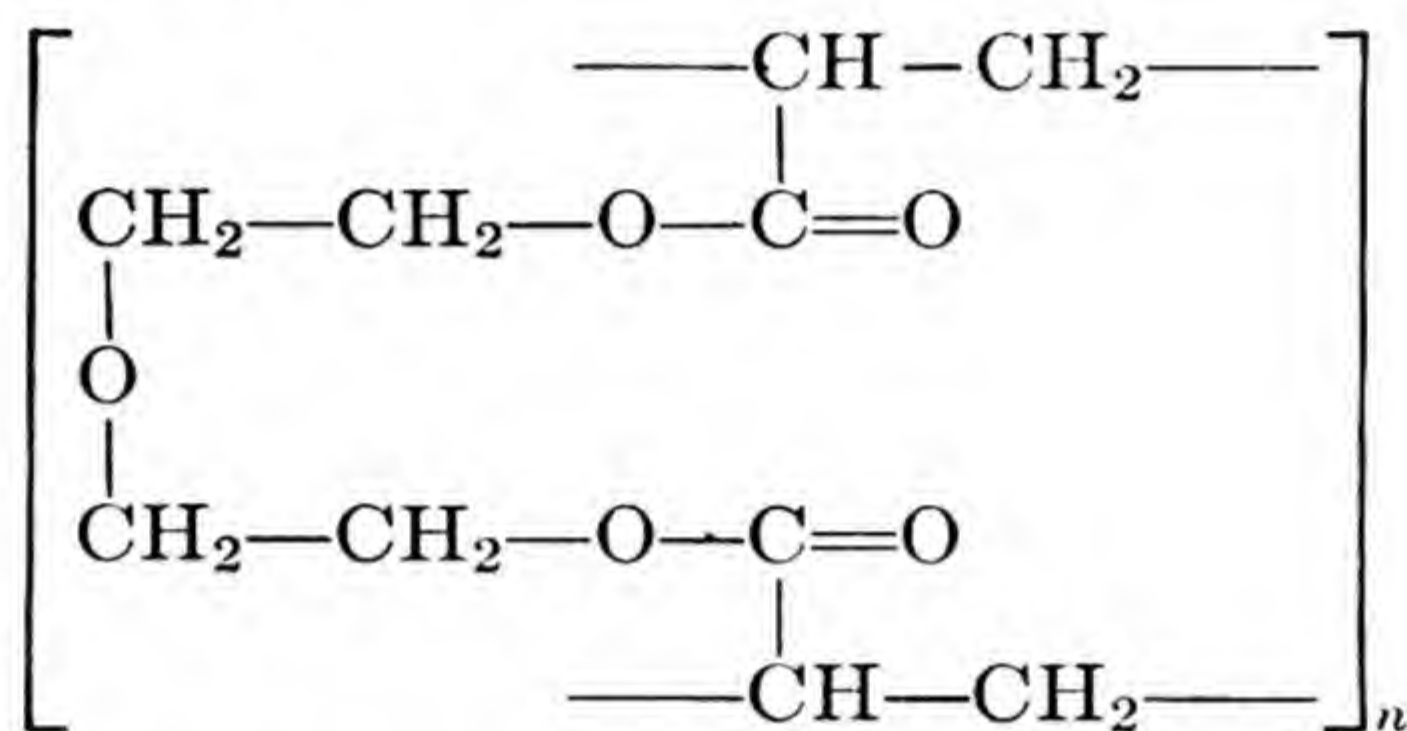
Similarly, from methacrylic acid, methyl-substituted divinyl compounds are formed that may be polymerized readily with peroxide catalysts, forming the cross-linked insoluble type of resins.

PROPERTIES AND USES OF DIVINYL RESINS

Advantages:

    Good transparency and clarity
    Availability in all colors
    Good hardness
    Good laminating adhesive

Disadvantages:

    High shrinkage
    Oxygen must be excluded during casting
    Low impact strength

Common uses:

    Laminating adhesive
    Casting sealant
    Lenses
    Cast sheets

COUMARONE-INDENE RESINS

Coumarone-indene resins were among the first synthetic resins developed commercially in the United States. They are produced from coal-tar light oils recovered from by-product coking operations. The fraction distilling

between 150 to 200°C. contains indene, coumarone, and homologous bodies, including their methyl derivatives. After careful distillation this fraction is treated with small quantities of concentrated sulfuric acid, which causes polymerization of the unsaturated coumarone and indene. The acid is settled and removed, the residue is neutralized and washed, and the naphthas are distilled off, leaving a viscous resin mixture at the distillation temperature (see Fig. 99). This resin is withdrawn from the kettle and solidified. The monomers are as follows:
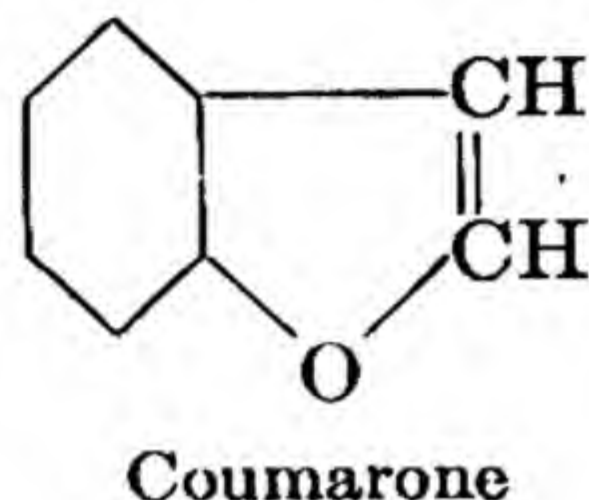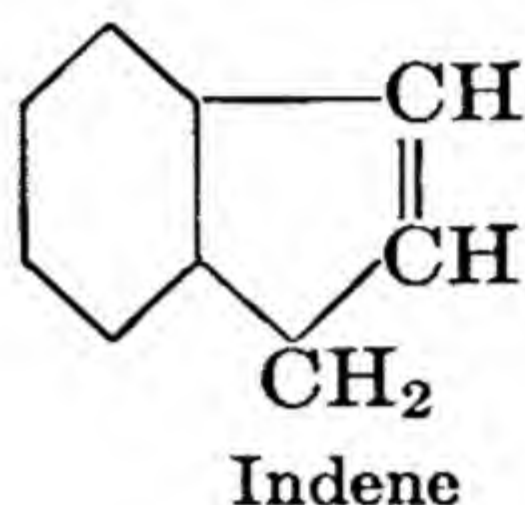
Indene

Coumarone

The polymer is assumed to have the following linear structure:
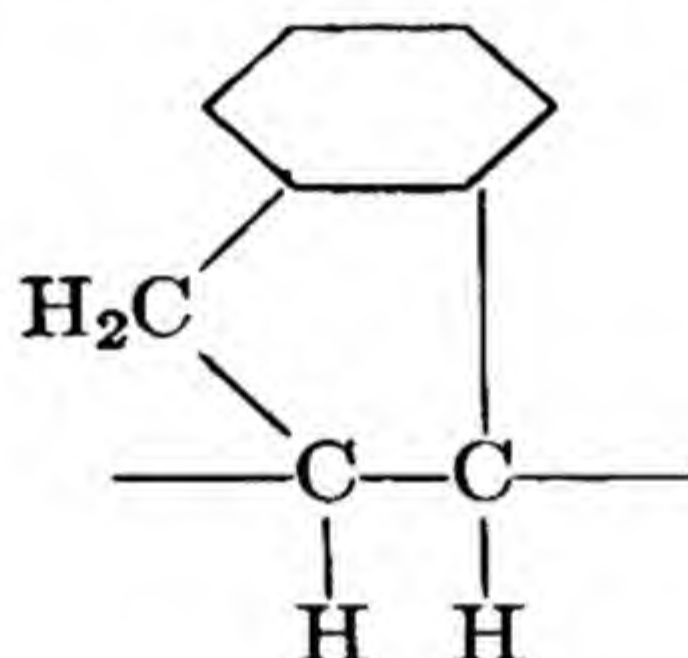
Coumarone-indene resins are compatible with a wide variety of resins and plasticizers. They have a relatively low molecular weight (the hardest has an average value near 1,000) and at temperatures above their melting points are completely fluid. These characteristics make them useful in modifying the properties of various plastic compositions.

Catalytic hydrogenation of the coumarone-indene polymers yields a series of resins that are described as cycloparaffin resins. They are more compatible with paraffin waxes and with aliphatic hydrocarbons than coumarone-indene polymers.

Para-coumarone-indene resins are used as a flux with some of the vinyl resins to improve the milling and flowing qualities and to decrease the cost of the finished plastic without too greatly sacrificing its properties. Coumarone-indene resins are also used in the manufacture of mastic floor tile, in which a themoplastic binder is employed. The resin is plasticized with various selected pitches or specially processed oils to give a binder of satisfactory physical properties and light color.

These resins are soluble in all aromatic hydrocarbons and most petroleum diluents up to the fraction boiling above 200°C. (392°F.). In general, the lower melting resins are more readily soluble in petroleum solvents. The

resins are also soluble in various vegetable and animal oils, with the exception of castor oil. In most cases, raw oils are better solvents than bodied, blown, or oxidized oils. Most esters, aldehydes, ketones, and chlorinated
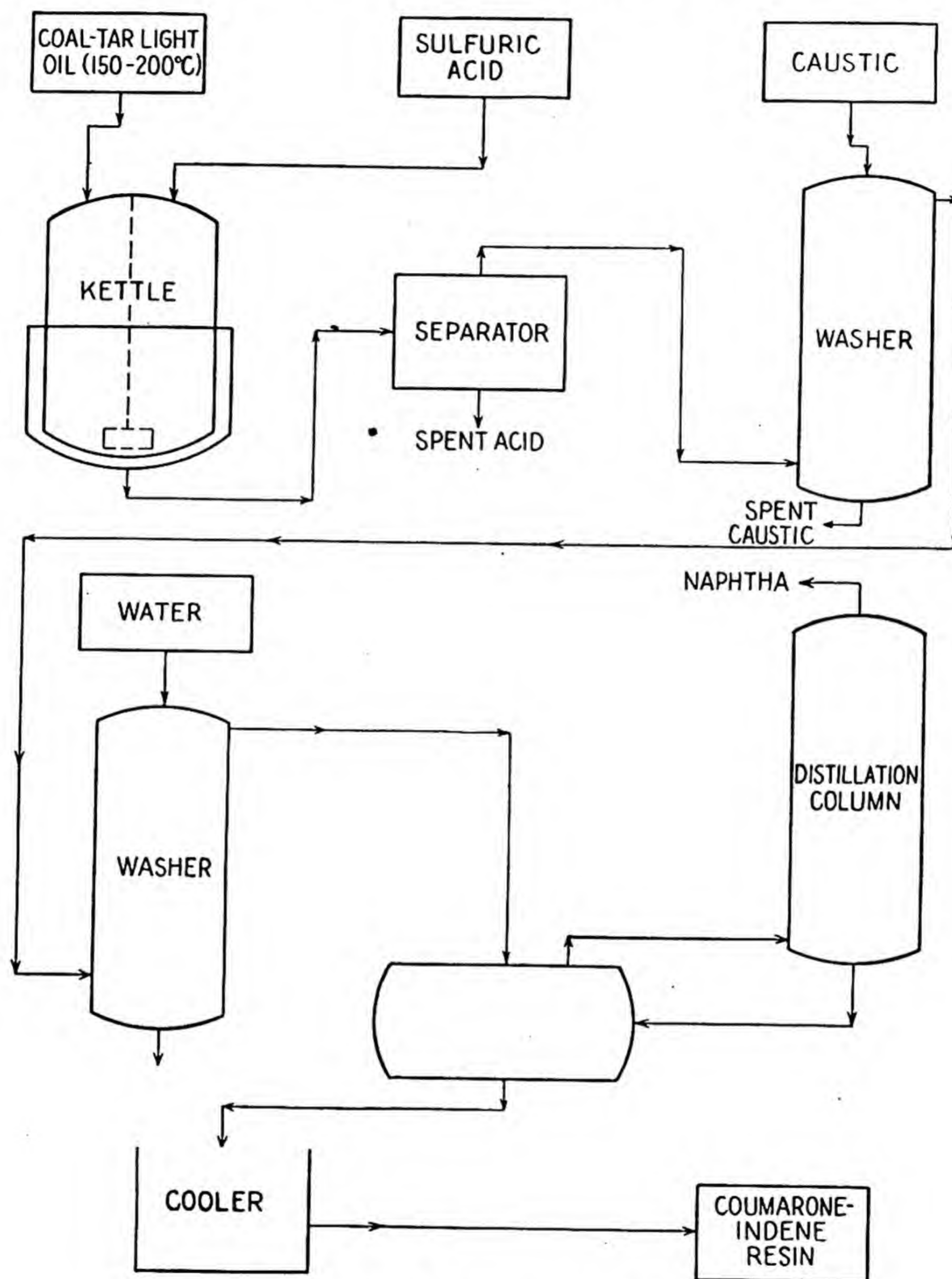
Fig. 99.—Flow sheet for coumarone-indene resins.

hydrocarbons are also good solvents for these unmodified resins. This high solubility permits the use of coumarone-indene resins in varnishes to replace the higher priced resins and to some extent ester gum. Their properties are inferior, however, and they are usually considered diluents.

The next largest use for coumarone-indene resins is in rubber compounding. Their effect is to soften the rubber during the milling. They are extensively used as binders and tackifiers in rubber compounding.

FUMARIC POLYMERS

Resins bearing similarity to those described in the preceding section are copolymers of fumaric acid esters with other selected monomers. The dialkyl fumarates polymerize in the presence of peroxide catalysts to form soft resins; however, a true copolymer having greatly improved properties results when polymerized together with vinyl acetate. The product is hard and when cast from dopes forms a tough film. Maleates, citroconates, and itaconates can be used in place of fumarates, and copolymerization can also be carried out with styrene.

PART VI

SILICONES

The development of the class of high polymers known as silicones in the United States in the early 1940's opened a new field of resins, plastic compounds, oils, and greases. The silicones differ in structure from all other classes of polymers in that the chain framework is composed of recurring silicon and oxygen atoms. This framework is modified and given special properties by the introduction of various organic radicals on the silicon atoms.

Strictly speaking, all the silicones cannot be called resins since some of them are fluids or resemble greases at temperatures considerably above room temperature. However, some types do exist in the resinous form and are becoming important in the field of plastics. Included among the various silicones now commercially available are fluids for use over a wide temperature range with relatively little change in viscosity, chemically resistant greases, insulating resins and varnishes, rubbers, high-temperature lubricants, and water repellents. Other types suitable for additional applications are under development.

In one sense, the basic structure of the silicones resembles that existing in quartz.[1] In the crystal of β-quartz each silicon atom is linked to four separate oxygen atoms, and each oxygen atom is in turn linked to two different silicon atoms. The resulting spiral siloxane chains thus are bound in a rigid assembly which, in terms of polymer chemistry, constitutes a completely cross-linked network of high melting point and low solubility. A single chain of alternate silicon and oxygen atoms has the following structure, but is linked through oxygen to similar chains at each silicon atom:
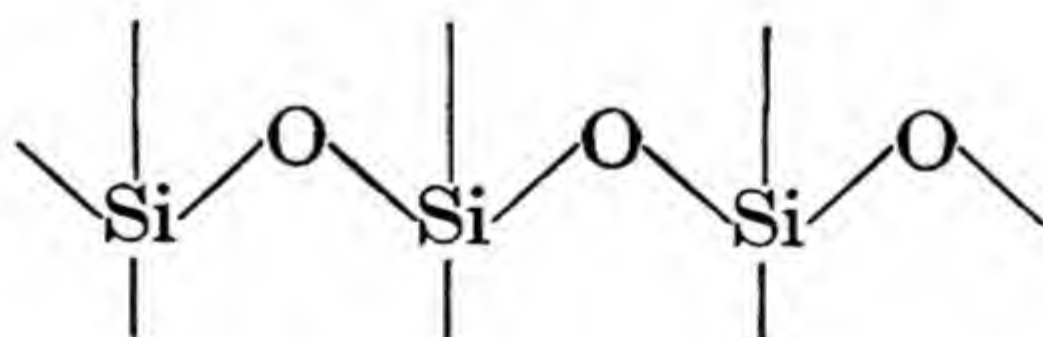
If a chain could be produced carrying two substituted organic groups on each silicon atom, cross linkage would be prevented and a linear or chain polymer would result.
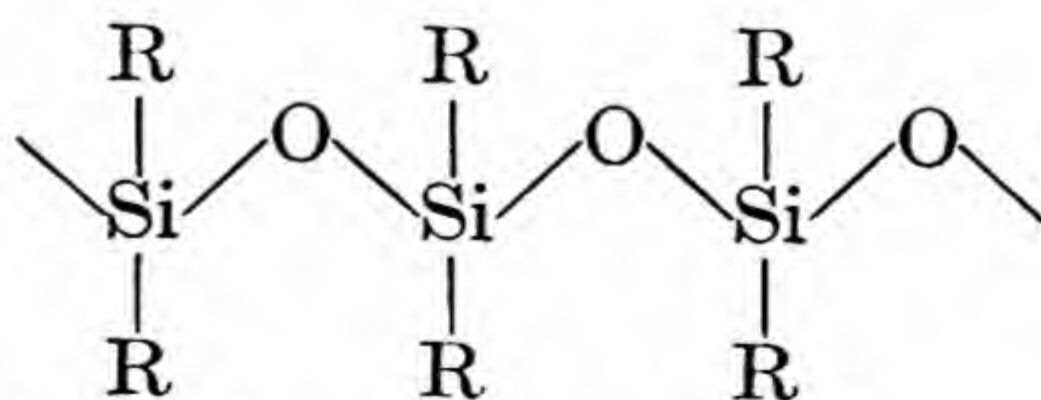
[1] ROCHOW, E. G., *Chem. Eng. News*, 23, 612 (1945).

This is a polyorganosiloxane, or silicone polymer. If the process of organic substitution purposely were left incomplete, such organosiloxane chains could be joined by oxygen bridges acting as cross links.
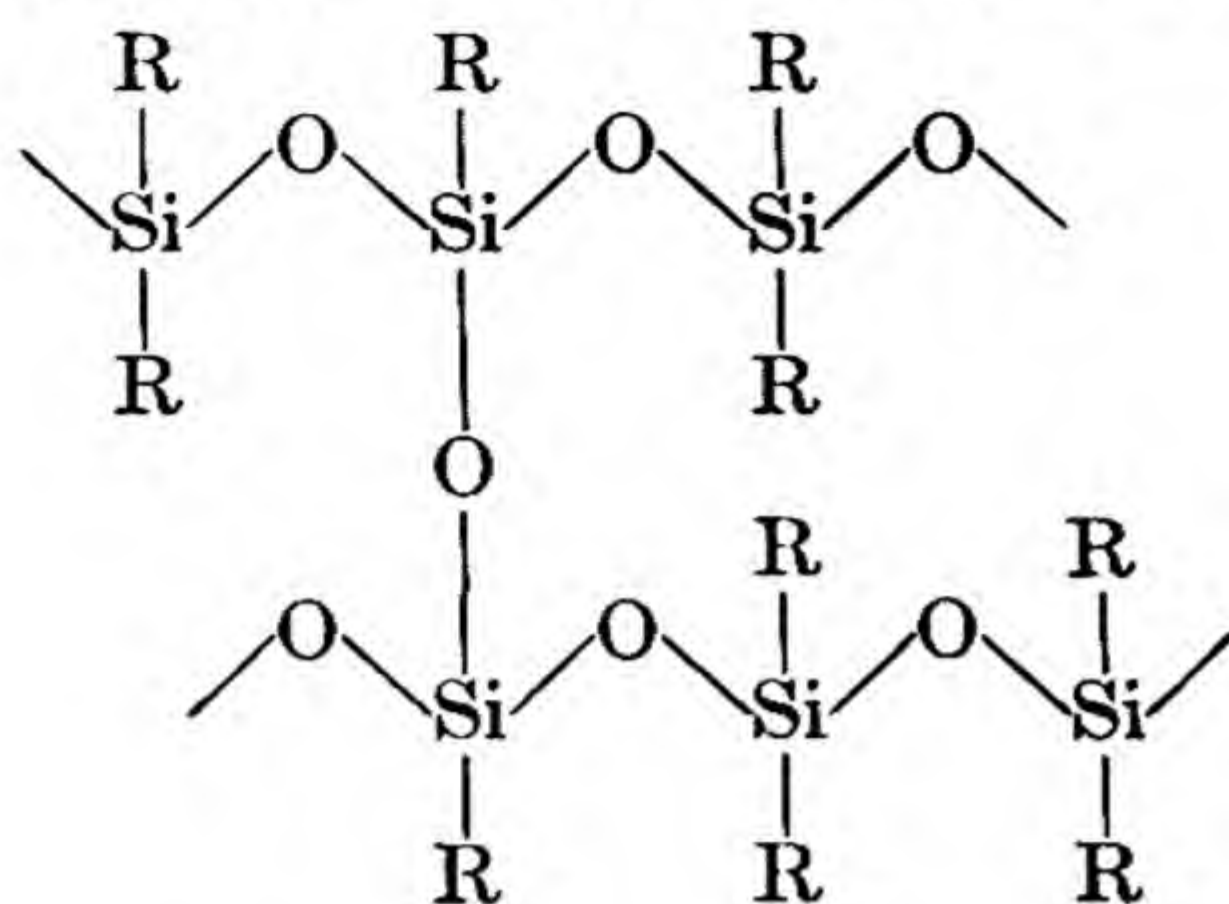
Similarly, tetrafunctional silicon atoms could be employed to establish a still higher degree of cross linking:[1]
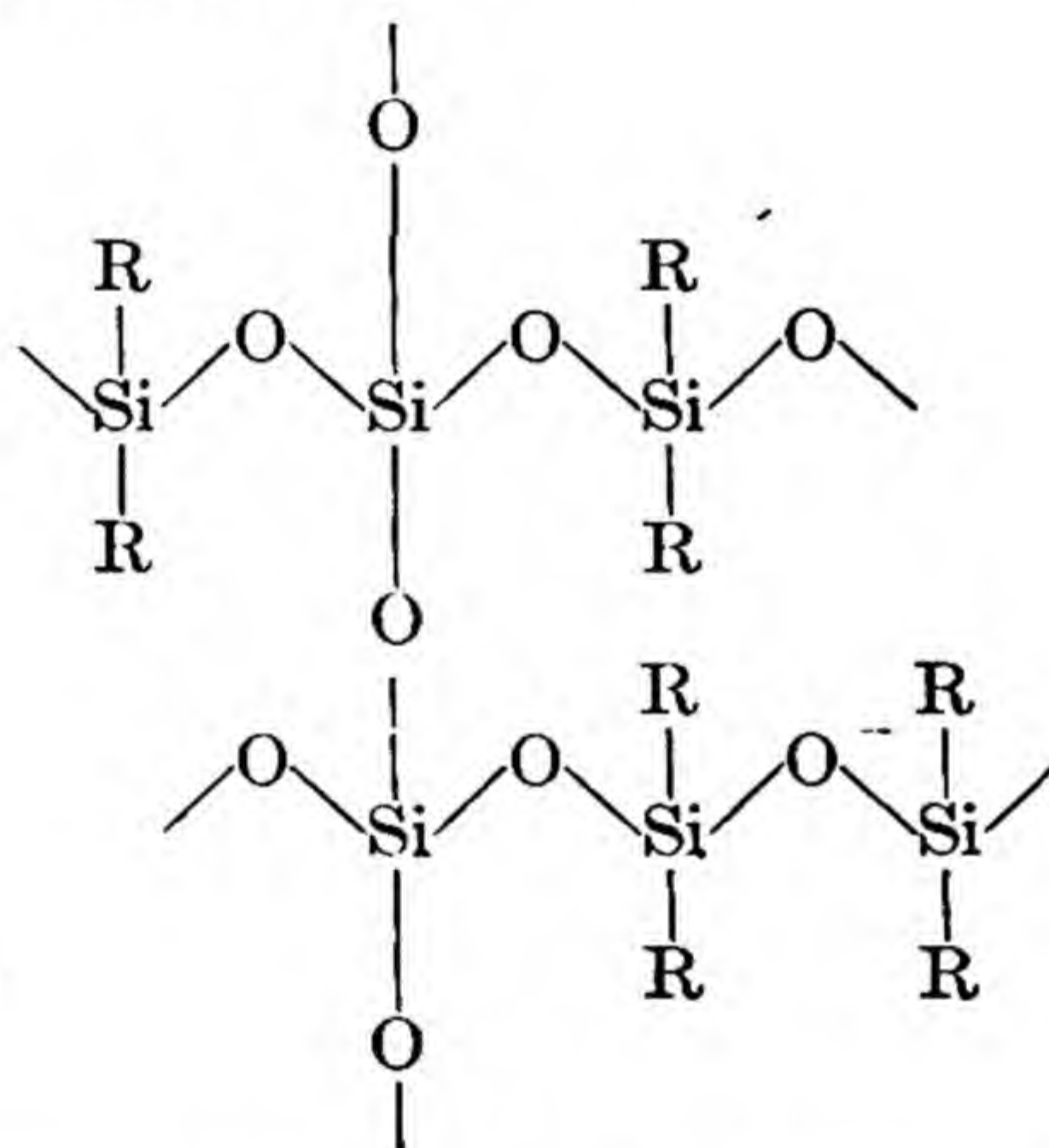
Thus there is a complete series of products theoretically possible, ranging from linear polymers that would be relatively soft and low-melting (in the case of the silicones, they are fluids at room temperature) to the very hard, high-melting quartz itself. The properties of the resins should then extend from those of true liquids, through the thermoplastic stage, then a rubbery state, and finally to a complex three-dimensional structure characterized by extreme heat-resistance, inertness, and hardness. This extreme range of properties is wider than the entire range of all the other synthetic resins and is the reason the silicones are classified as a separate and entire class in themselves. It should be realized, however, that the actual grades of silicone resins now in production are only relatively isolated members of this much larger class, and production as well as technical difficulties may

[1] *Ibid.*

prevent the development of resins throughout the complete range of properties.

From the foregoing it may be concluded that the degree of organic substitution determines the extent of cross linking, which in turn governs the properties of the polymer. Solubility, fusibility, hardness,. etc., may be expected to depend primarily on the degree of cross linking, but the mechanical and chemical properties will change with the kind or kinds of radicals that are attached to the silicon. Thus the properties will vary with the type of substituent groups, the R/Si ratio, and the degree of polymerization. These structural possibilities might be compared to the ethenic compounds, in which polyethylene forms the parent chain and all the other resins are formed by substituting organic radicals for hydrogen.

As an example of the above, methyl silicone is in reality a general name for products of varying properties, from oils to elastomers. The oils are composed of linear chains of relatively low molecular weight; resins are formed by cross-linked structures; and elastomers are very high molecular-weight products.

Although dimethyldichlorosilane, $(CH_3)_2SiCl_2$, is the principal raw material for all these products, modifications produced by varying reaction conditions and adding controlled amounts of other silanes have a great influence on the product produced. If a mixture of di- and trimethyl-chlorosilane is hydrolyzed, the chief product is a linear polymer in which the chains of dimethylsiloxane units are terminated by monofunctional trimethyl units as follows:

$$(CH_3)_3Si \ [(CH_3)_2SiO]_n \ OSi(CH_3)_3$$
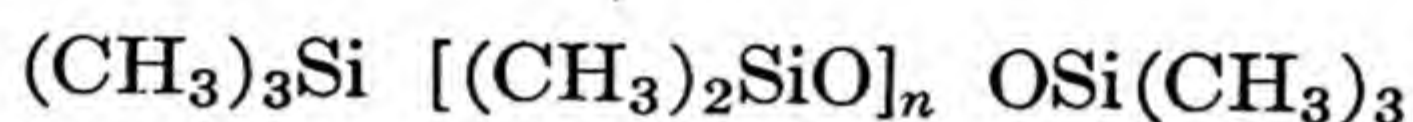
The trimethylsiloxane units "cap" the ends of the chains, preventing further condensation and imparting a high degree of chemical stability.[1] The resulting products are highly stable oils that are not affected by high temperatures and most chemicals. These linear methyl polysiloxanes are the basis of the "silicone oils" or fluids.

These products may also be prepared by a catalytic rearrangement of monofunctional and difunctional siloxane units.[2] Polydimethylsiloxane is mixed with the proper proportion of hexamethyldisiloxane, $(CH_3)_3SiOSi-(CH_3)_3$, and about 4 per cent by volume of concentrated sulfuric acid is added. The sulfuric acid appears to react with the siloxane bond to form sulfate esters and water; the sulfate esters then hydrolyze, and the regenerated sulfuric acid attacks another siloxane bond. In this way, siloxane bonds are opened and closed at random until an equilibrium distribution of chain lengths is obtained. The average chain length is determined by

[1] ROCHOW, E. G., "Introduction to Chemistry of the Silicones," John Wiley & Sons, Inc., New York, 1946.

[2] PATNODE, W. I., *J. Am. Chem. Soc.*, **67**, 68,358 (1946).

the proportions of reagents.   The oil is washed and neutralized, and a stable product results.

These methyl silicone oils have flow points as low as $-85°C$. and may be used at $150°C$. without oxidation or sludging.   They also have a much smaller change of viscosity with temperature than any petroleum lubricant, making them ideal oils for hydraulic systems that are exposed to wide temperature variations.

The rubbers are made by what is in effect a polymerization of previously prepared linear dimethyl chains.   The dimethyl polymer is treated with a
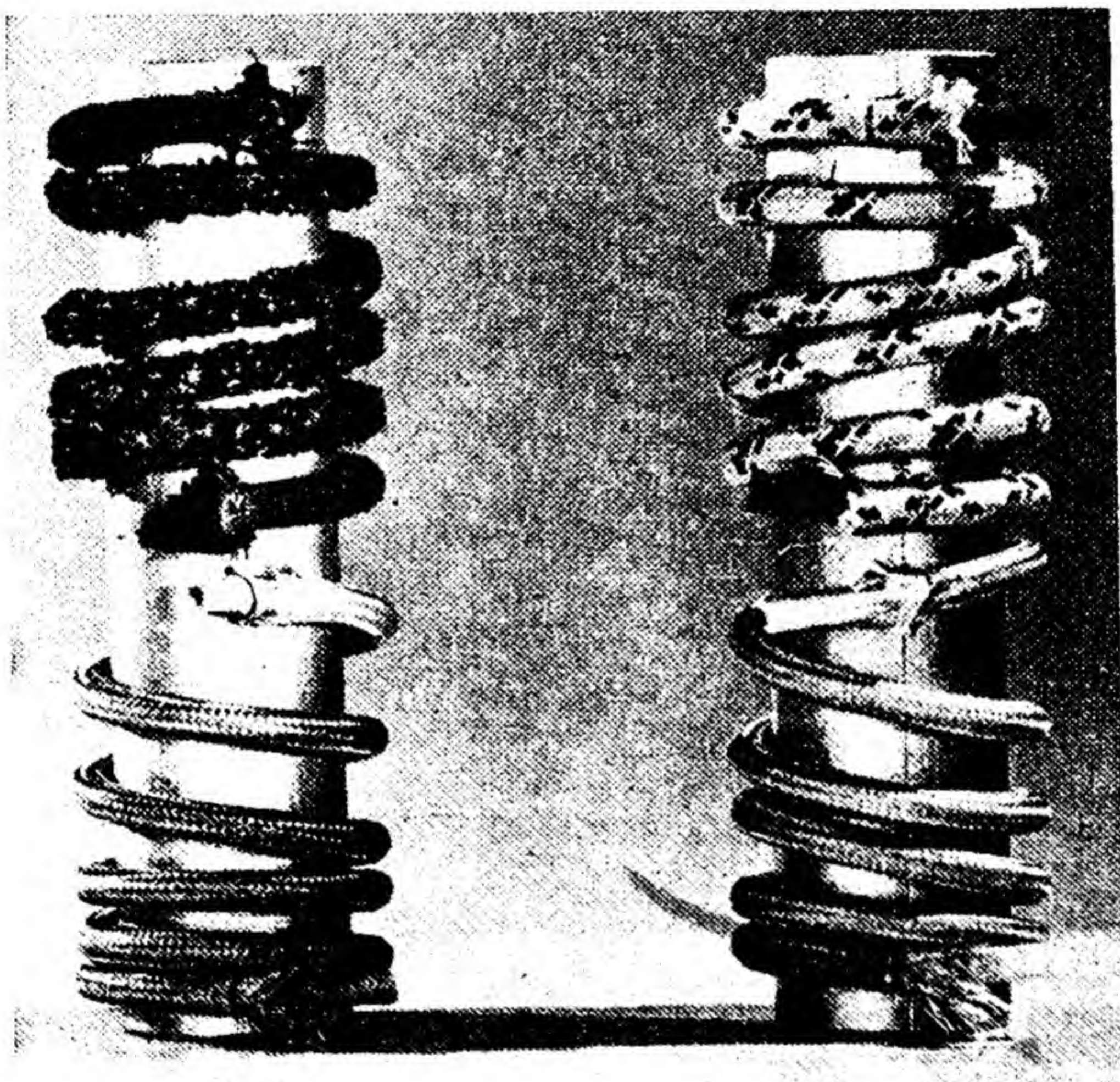
Fig. 100.—A comparison of silicone and rubber insulation.   The tube at the right has been exposed to a temperature of $50°C$. and that at the left to $250°C$.   The silicone insulation is not affected, whereas the rubber has been destroyed.   (*Dow Corning Corp.*)

reagent that opens a few silicon–oxygen bonds in a manner similar to the action of sulfuric acid previously described.   Since no trifunctional groups are present, no cross linking occurs, and the opened bonds continue to unite with one another until aggregates of two thousand or more dimethylsiloxane units are formed.   The elastomer is milled with inorganic fillers on mixing rolls, and a curing catalyst is added.   Although the mechanical properties are not so satisfactory as those of other rubbers, it is well suited to applications where thermal stability and resistance to chemical reagents are more important than tensile strength or tear resistance (see Fig. 100).

The methyl silicone resins require cross linking to attain their resinous state. Their properties are dependent on their molecular weight and the degree of cross linking. The ratio of methyl groups to silicon is a measure of the amount of cross linkage and serves as a convenient means of indexing various products. CH_3/Si ratios of 1.2, 1.3, 1.4, and 1.5 give colorless solids with densities decreasing from 1.20 to 1.06.[1] The time required to harden them at 100°C. increases from 2 to 24 hr. Below 1.2 methyl groups per silicon atom, the resins are sticky sirups that cure to hard, brittle, glassy masses. Above a ratio of 1.7, the products are oily and relatively volatile.

The methyl silicone resins have excellent heat-resistant properties. Samples have remained unchanged over long periods at 200°C. Above 300°C., slow oxidation takes place in the presence of air. Since these resins do not carbonize or leave a carbonaceous residue, they are particularly well suited as electrical insulating materials as breakdown of organic insulators is usually associated with carbonization. In addition, they have excellent electrical characteristics for insulating materials both in the solid form and as an impregnating material for glass cloth. These properties, together with their thermal stability and noncharring characteristics, indicate a wide field of usefulness as electrical insulating materials.

OTHER ALKYL SILICONE RESINS

The ethyl group attached to silicon in place of the methyl group in a siloxane chain produces a softer, more soluble, and slower curing product.[2] A ratio of two ethyl groups per silicon atom gives a linear polymer that is an oil, regardless of the molecular weight. A ratio of CH_3 to Si of one produces products that are suitable for coating compositions. Propyl, butyl, and amyl silicones of the type $(R_2SiO)_n$ are colorless oily liquids that resemble ethyl silicone in appearance. In general, the larger alkyl groups cause the resin to cure more slowly, to remain softer, and to oxidize more readily.

ARYL SILICONES

The hydrolysis of diphenyldichlorosilane produces the diol, $(C_6H_5)_2$-$Si(OH)_2$, which can be isolated since it does not immediately condense as does the methyl derivative. Controlled condensation produces the cyclic trimer and tetramer, but it can be condensed to produce a brittle and rather weak higher polymer with a resinous character. This product burns readily but is very resistant to oxidation. If chlorinated phenyl groups

[1] ROCHOW, E. G., and W. F. GILLIAM, *J. Am. Chem. Soc.*, **63**, 798 (1941).

[2] ROCHOW, E. G., "Introduction to Chemistry of the Silicones," John Wiley & Sons Inc., New York, 1946.

are used, the flammability is reduced.[1] Other aryl derivatives resemble the phenyl silicones, with some variation in properties.

MIXED SILICONES

The alkyl silicones of high R/Si ratios are oily liquids. Resinous properties are produced by a considerable amount of cross linkage, resulting in a much lower R/Si ratio. Aryl silicones, on the other hand, are brittle weak solids even with high R/Si ratios. By attaching both alkyl and phenyl groups to the same silicon atom or by cocondensing alkyl and phenyl silicols to make a copolymer, resins have been produced with advantageous intermediate properties. Marked mprovements are produced in strength and toughness. Thus the most important resins now in production are mixed methyl-phenyl and ethyl-phenyl siloxanes plus the previously described cross-linked methyl silicones.

METHODS OF PRODUCTION

The Grignard Method.—The monomers are prepared from silicon tetrachloride by the stepwise substitution of chlorine by the Grignard reaction (see Fig. 101).

$$C_2H_5MgCl + SiCl_4 \longrightarrow C_2H_5SiCl_3 + MgCl_2$$

$$C_2H_5MgCl + C_2H_5SiCl_3 \longrightarrow (C_2H_5)_2SiCl_2 + MgCl_2$$

Mono- and tetrachlorosilanes are also produced and excess silicon tetrachloride remains in the reaction products. This mixture is first separated from the magnesium chloride and then distilled to remove the solvent and to separate the various components. The monochloride may be recycled to add one more alkyl group to produce the desired dichloride. In the case of the methyl derivative, the trichloride can be used to produce cross-linked resins.

The Direct Method.—The Grignard method has been operated successfully on a commercial basis, but, theoretically at least, has some important disadvantages. The ratio of raw materials required to final product produced is high; the by-product magnesium chloride has little value; very reactive Grignard solutions must be handled; a volatile, inflammable solvent is used; and the magnesium chloride must be removed from a mixture that must be kept anhydrous.

Some of the disadvantages are avoided by the so-called "direct" process[2]

[1] ROCHOW, E. G., U. S. Patent 2,258,219.
[2] ROCHOW, E. G., J. Am. Chem. Soc., 67, 963 (1945).

in which an organic chloride reacts with elementary silicon in the presence of a copper catalyst.

$$2RCl + Si \xrightarrow{Cu} R_2SiCl_2$$
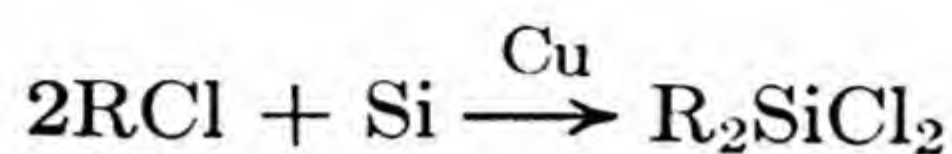
This reaction also produces mono- and trichlorosilanes as well as silicon
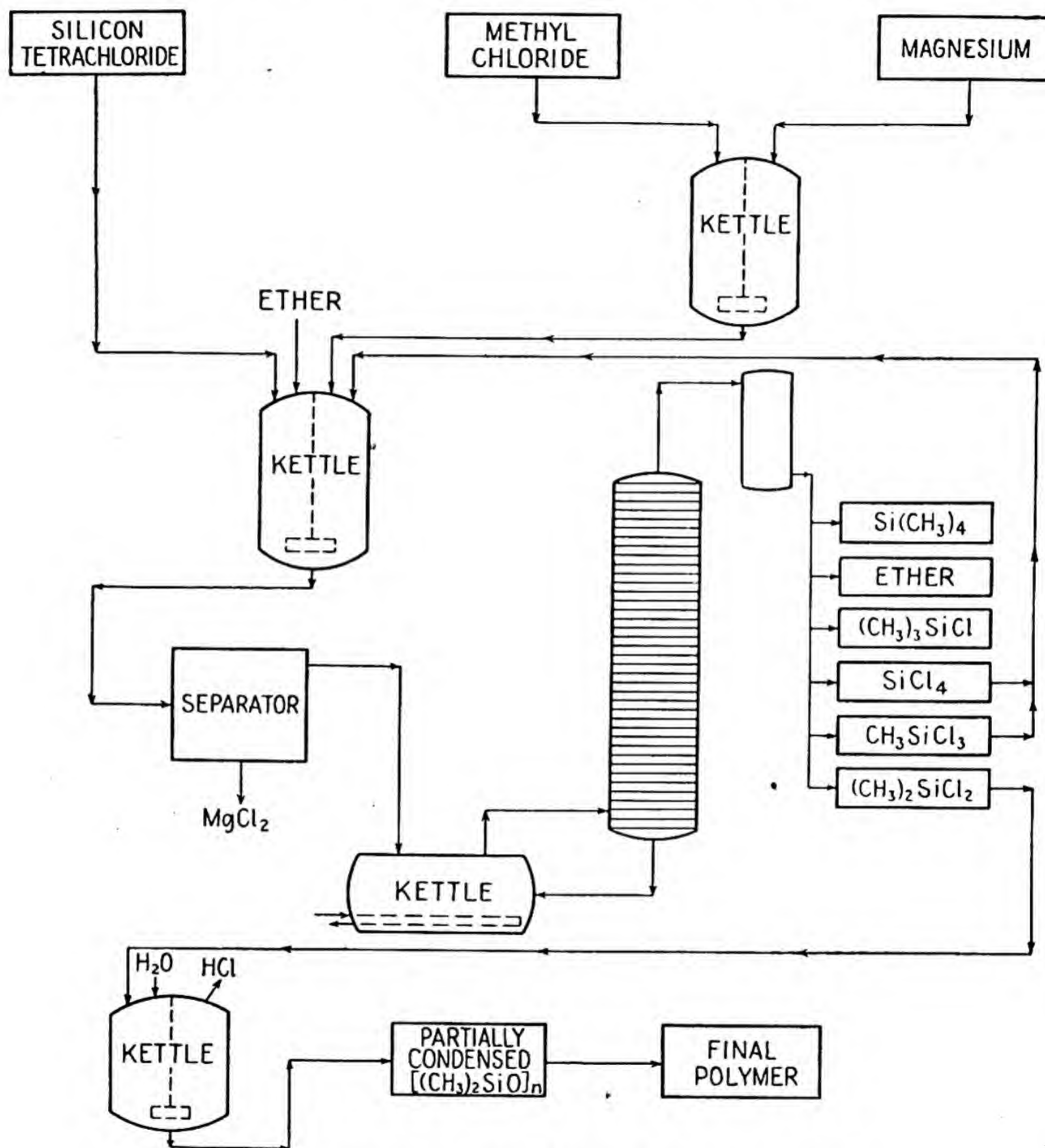
FIG. 101.—Silicone production by the Grignard method.

tetrachloride and a number of other compounds, all of which must be separated by distillation as in the Grignard method. Copper equivalent to about 10 per cent of the weight of the silicon is employed as catalyst. Silver has been used in the preparation of phenyl silicon chlorides.

The disubstituted organosilicon chlorides may be hydrolyzed to the cor-
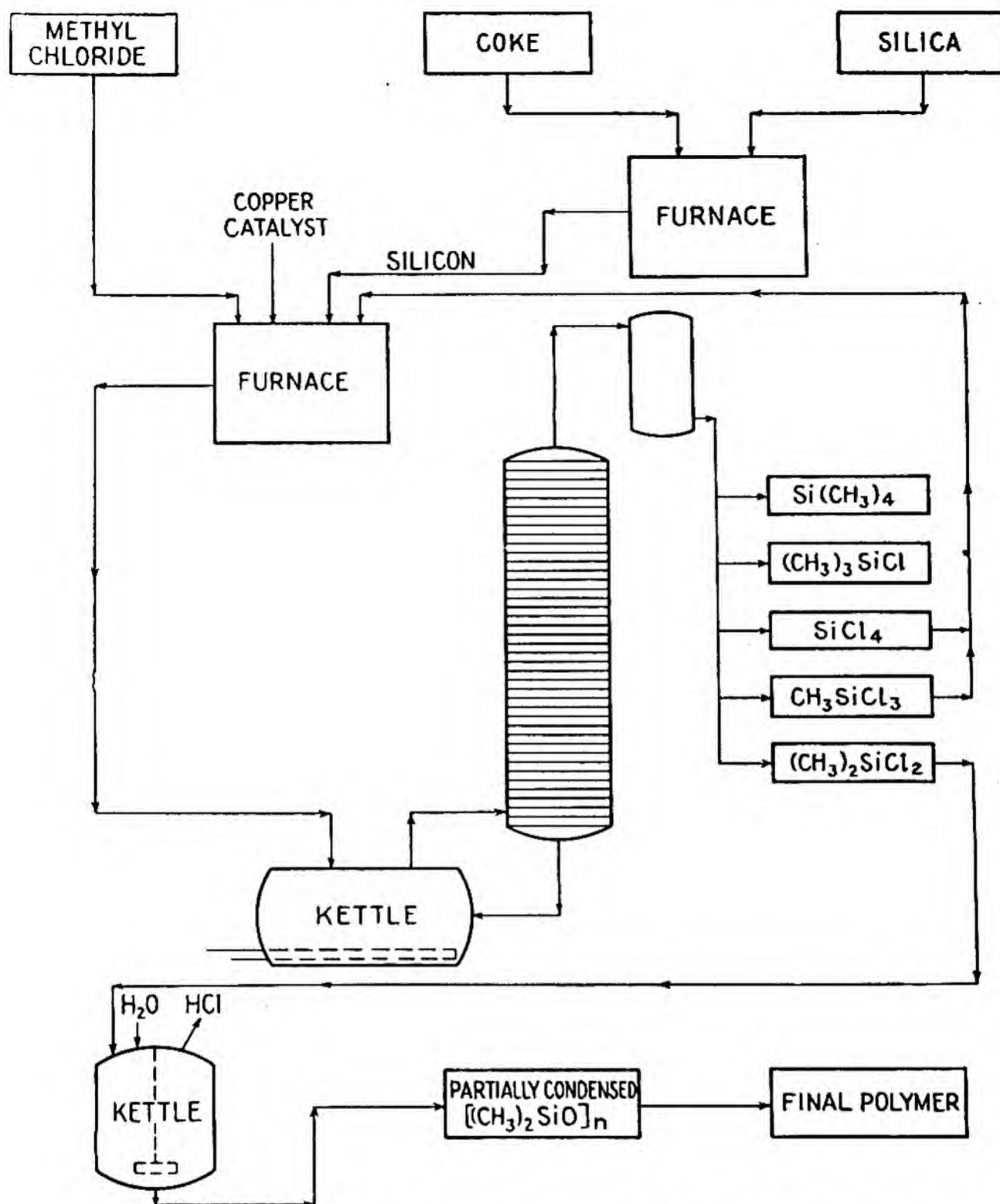
FIG. 102.—Flow sheet for the direct process for silicone production.

responding hydroxy compounds to produce silicones as shown on the flow sheet (see Fig. 102).

$$(C_2H_5)_2SiCl_2 + 2H_2O \longrightarrow (C_2H_5)_2Si(OH)_2 + 2HCl$$

$$(C_2H_5)_2Si(OH)_2 \longrightarrow \left[-\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{Si}} - O - \right]_n$$
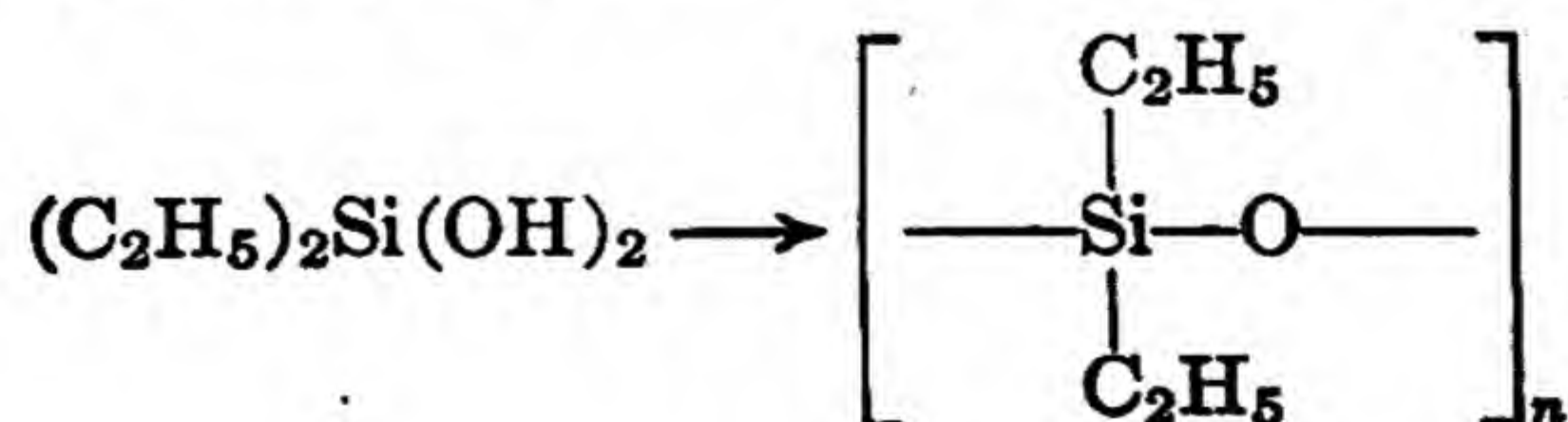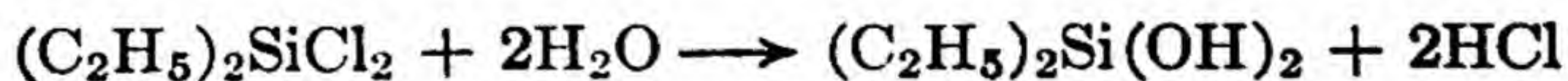
The phenyl-substituted polymer would have the following structure:

$$
\left[\quad \text{—Si—O—} \quad \right]_n
$$
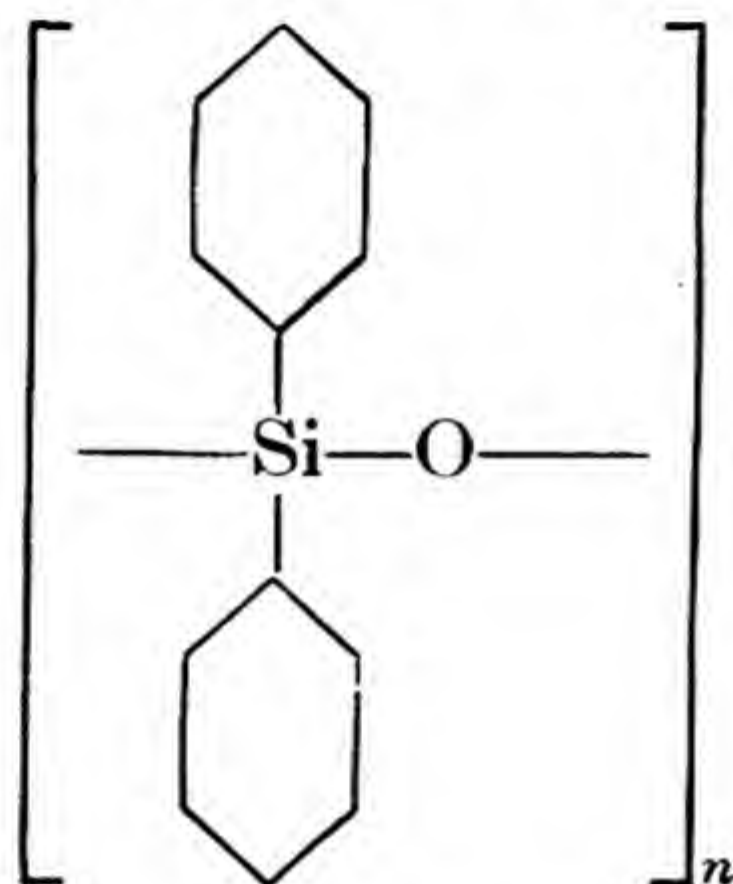
Cross linking of linear chains is accomplished by hydrolyzing a mono-substituted silicon chloride along with the disubstituted compound, thereby introducing $RSi(OH)_3$ molecules into the condensing mass.

$$
\begin{array}{c}
RSi(OH)_3 \ + \\
R_2Si(OH)_2 \longrightarrow
\end{array}
$$
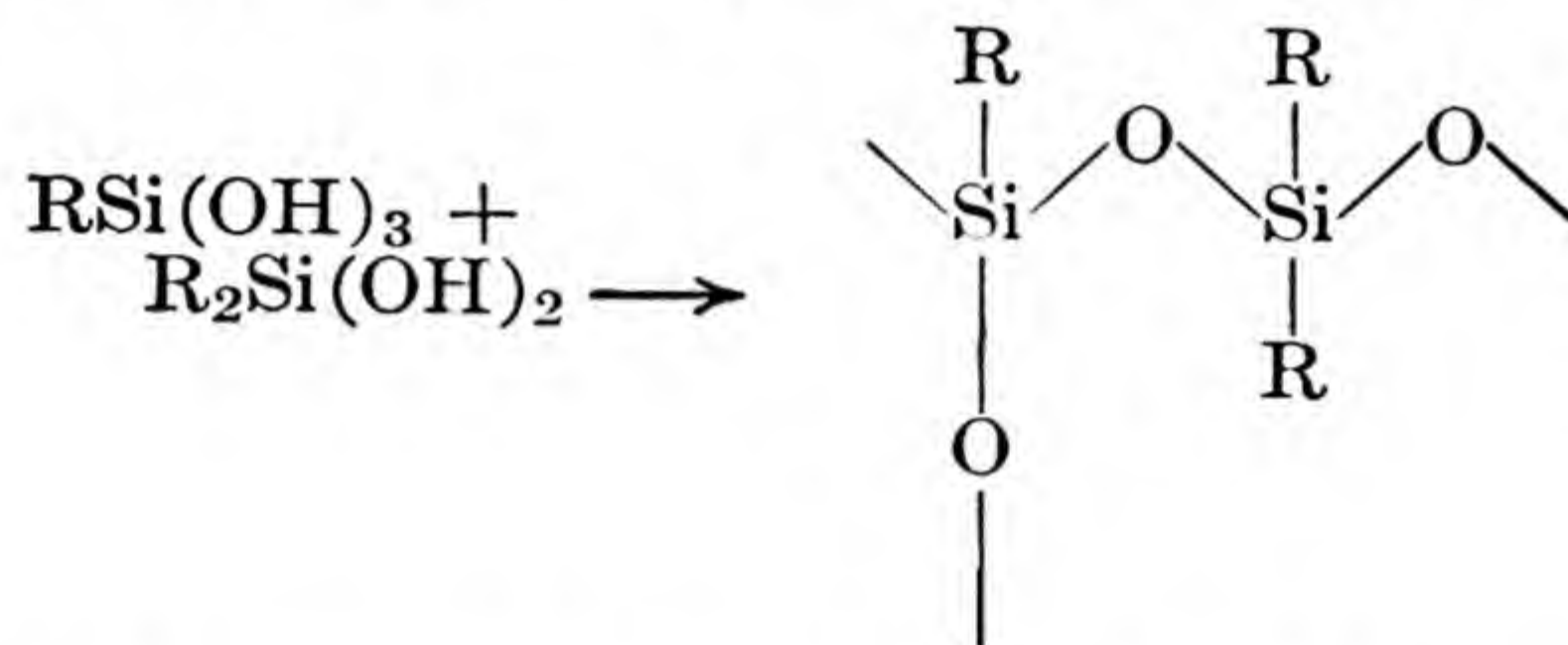
Silicon tetrachloride may also be added within low limits, usually 5 to 20 per cent. If added in higher concentrations, silicon dioxide forms before cocondensation can occur. The silicon tetrachloride hydrolyzes to the hypothetical silicic acid, but instead of condensing to silica this condenses intermolecularly with the diol.

$$
\begin{array}{c}
Si(OH)_4 \ + \\
R_2Si(OH)_2 \longrightarrow
\end{array}
$$
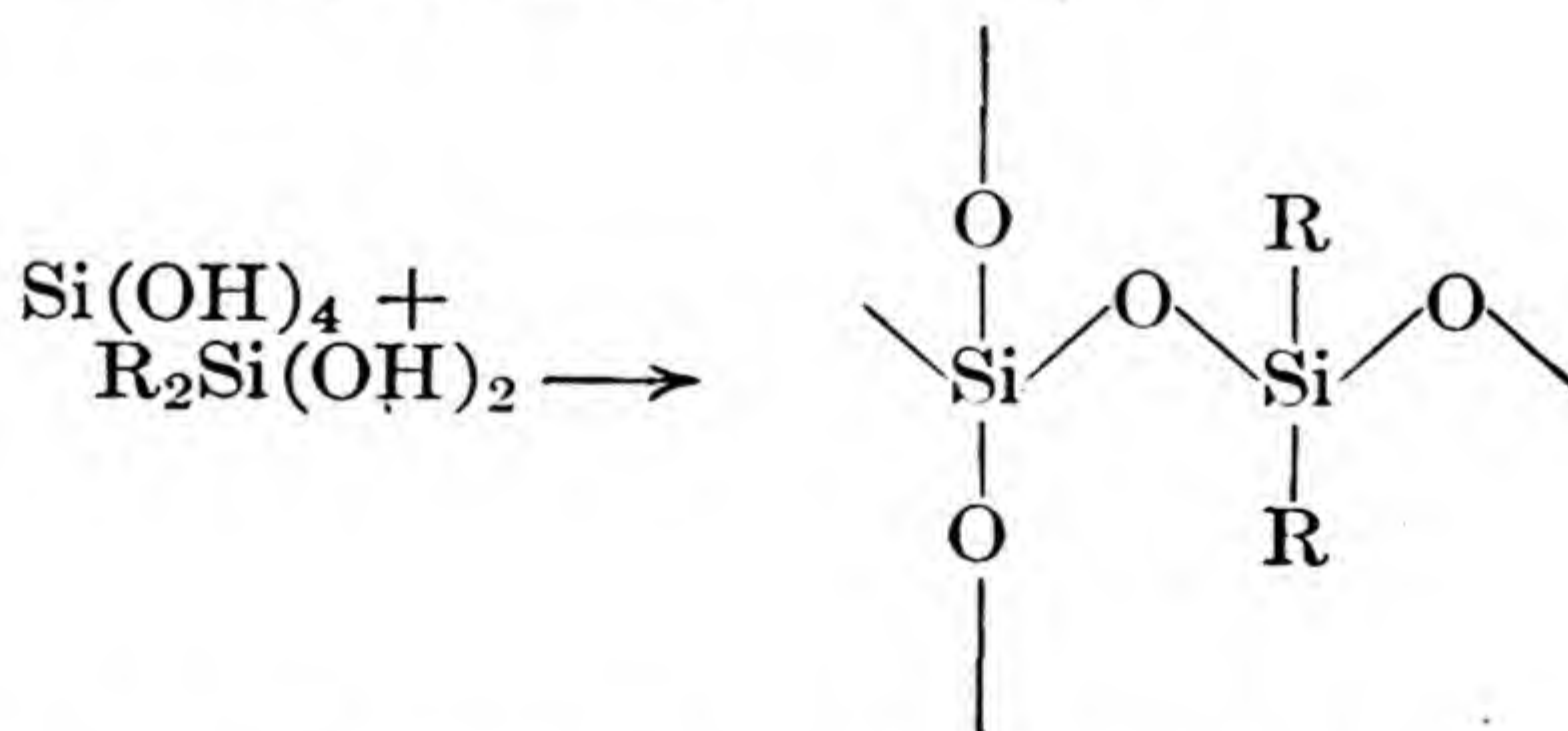
The result is a double cross linking wherever an $Si(OH)_4$ has gone into the structure.

Methyl silicone polymers are commercially available in the form of oils and elastomers, both of which are useful at temperatures above those permissible for their organic counterparts. The oils have flow points as low as $-85°C$. and may be used at $+150°C$. without oxidation or sludging;

their most unusual property is their small change of viscosity with temperature. The elastomers may be compounded and molded to produce a silicone "rubber" that does not decompose at $+300°C$. nor harden at $-55°C$. and maintains its elasticity over long periods of time at $150°$ under load.[1] Of particular interest for its surprising behavior is that methyl silicone polymer which is known as "bouncing putty," a material that is plastic to slowly applied forces. Under static load, even its own weight,
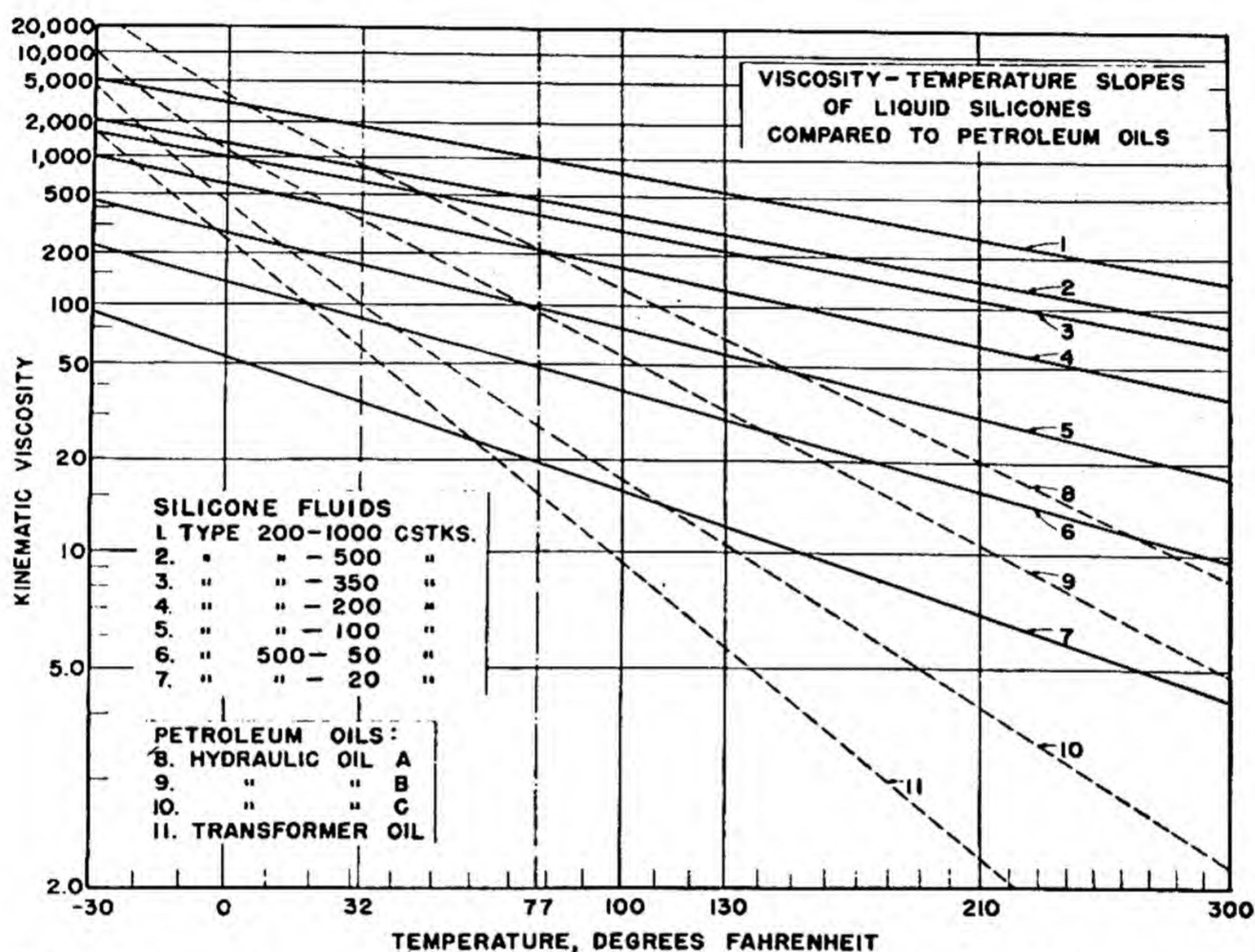
FIG. 103.—A comparison of the temperature-viscosity characteristics of silicone fluids and hydrocarbon oils. (*The Dow Corning Corp.*)

this composition deforms and flows like a viscous liquid, but when struck or thrown it rebounds like a high-grade rubber. No explanation has been given for the importance of the time factor in this elastic behavior.

Silicone fluids are available that are useful wherever there is a need for a liquid with a lower rate of change of viscosity at low temperatures or practical nonvolatility at elevated temperatures (see Fig. 103). These properties, together with the inertness of the liquids toward metals, coatings, and gasketing materials, indicate uses as damping fluids, gauge fluids, and dashpot liquids. Because of their exceptional resistance to chemicals, they have also proved useful as impregnants for asbestos packing and gaskets in chemical pumps.

[1] ROCHOW, E. G., *Chem. Eng. News*, **23**, 612 (1945).

The silicone fluids can also be used as liquid dielectrics, because of their extremely low power loss, low water absorption, and stability to heat. Their solutions in chlorinated solvents may be used in treating the surfaces of glass and ceramic insulating forms to render them water repellent to prevent loss of resistivity due to moisture.

Exposure of various materials to the vapors of organosilicon halides can also be used to develop a water-repellent film of silicone on the surface (see Fig. 104). Vapors of chlorosilane react with adsorbed moisture on the surface to be treated, forming a silicone layer.[1] Ceramic articles to be treated are preconditioned at 50 to 90 per cent relative humidity, exposed a few minutes to the vapors of the chlorosilane, and then aired to allow
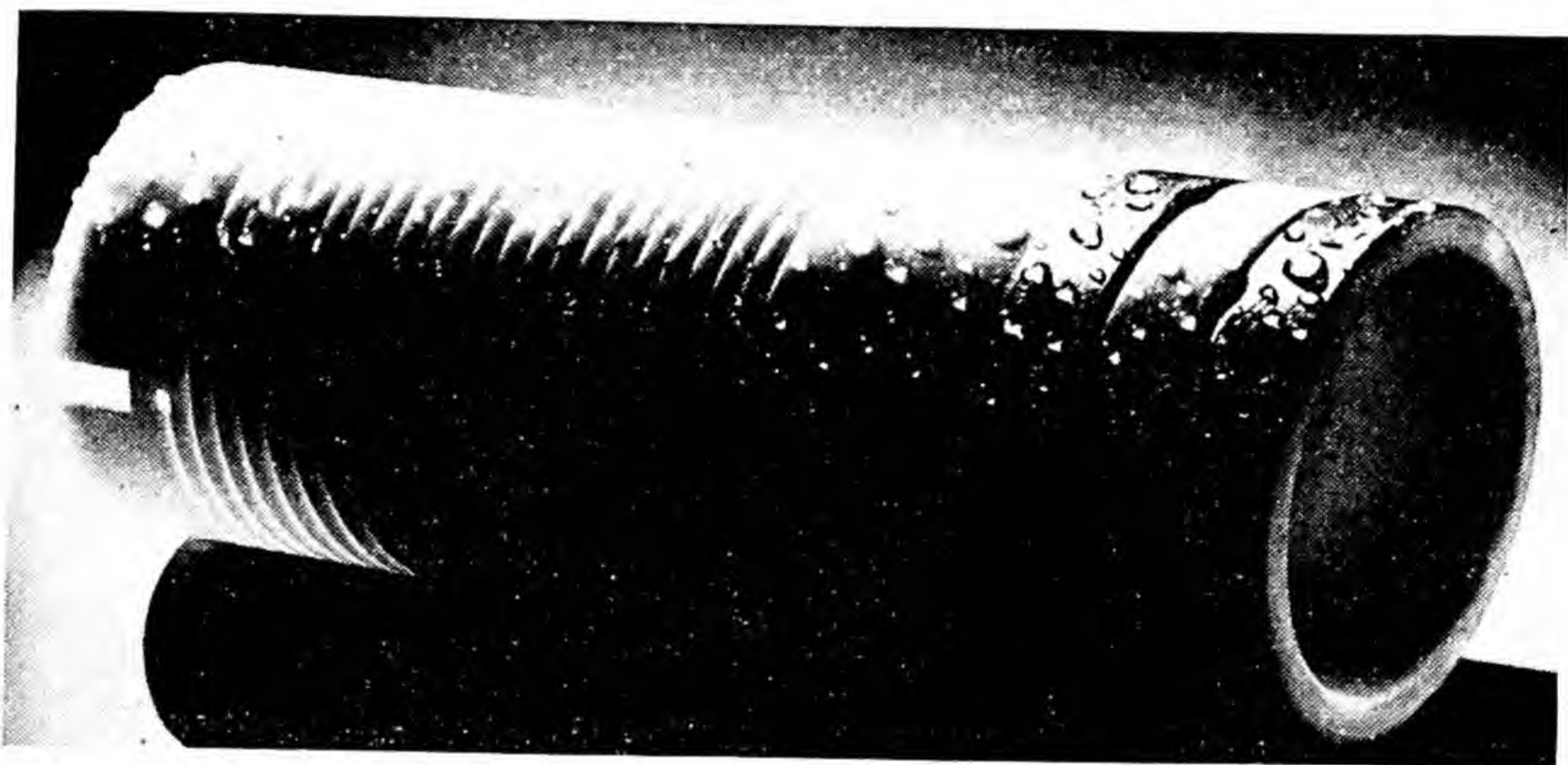
FIG. 104.—A coil form that has been made water repellent by treatment with chlorosilane vapors. (*Dow Corning Corp.*)

the by-produced hydrochloric acid to volatilize. Treated surfaces show a high angle of contact for water droplets. Moisture does not condense on such a surface as a continuous film but as small isolated droplets. The electrical resistance of surfaces so treated remains high even under humid conditions.

Various types of greases are available for special lubrication problems. Different grades are available to permit a total range of working temperatures from $-70°F.$ to as high as $400°F.$, a much wider range than can be covered with other conventional greases. Special plug-cock grease is available for use in contact with chemicals that dissolve other greases or for severe temperature conditions. A variety of this grease is marketed as a stopcock grease for laboratory glassware.

One of the most important applications of the silicone resins up to this time has been for electrical insulation. Since they are not affected by

[1] PATNODE, W. I., U. S. Patent 2,306,222 (1942).

temperatures that cause burning or charring of organic resins and varnishes, they are combined with glass fibers or cloth, asbestos, or mica to produce insulating materials for electric motors, coils, etc., that are more reliable and safer. Since motors can be permitted to run hotter with this type of insulation, they can be made much smaller because more heat can be dissipated per unit weight or surface. Motors can also be installed in hotter zones, such as those in hot air ducts, if the insulation will withstand the temperature.

The largest single use has been for the preparation of an electrical insulating paste that is used to fill the sleeves of aircraft spark plugs.[1] The paste eliminates air in the sleeves which would cause them to burst at high altitudes and, since it is completely water repellent, enables safe flight in extremely moist conditions. Many other uses of this paste have been made where a soft insulating material is required that is not affected by temperature or moisture.

Projected uses are for high-temperature enamels, special inert coatings, and inert rubbers and rubberlike materials. Silicone rubbers are in use at the present time for high-temperature gaskets, such as those required in the powerful Navy searchlights, and for gaskets for chemical equipment.

The greatest limitation to the extended use of silicones is their high cost. This will not interfere with their use, however, in those instances where longer life or extreme conditions warrant their application, and recent developments indicate that costs of production may be materially lowered.

[1] COLLINGS, W. R., *Chem. Eng. News*, **23**, 1616 (1945).

PART VII

RUBBER AND SYNTHETIC RUBBERS

Certain tropical and semitropical trees and shrubs yield a white liquid of milklike appearance called "latex." When this milklike liquid is evaporated or coagulated, rubber is produced. Whatever may be the tree's purpose in forming latex, it has not been discovered, but the product, obtained by coagulation, treatment, and working, is an important commodity of modern civilization. There is a divergence of botanical opinion, but it is generally supposed that latex acts either as a food-storage reservoir or as a means of discouraging insect pests and parasites from biting or boring into the tree, since the latex heals and seals any wounds inflicted on the bark.

The main source of rubber is the rubber tree, *Hevea brasiliensis*. The rubber exists in the tree in the form of a milky latex consisting of colloidal globules about 0.09 to 1.85 microns in diameter suspended in an aqueous medium. This latex is contained in the inner bark and is entirely separate from the sap. The composition of the latex is approximately as follows:

Water.. 60%
Rubber... 35%
Proteins.. 2%
Fatty materials... 1%
Quebrachitol.. 1%
Inorganic salts... 0.4%

The empirical formula of the rubber hydrocarbon is $(C_5H_8)_n$, where the degree of polymerization n is of the order of 2,000. It has been proved that the parent chemical compound that forms the rubber structure is isoprene

$$CH_2\!=\!C\!-\!CH\!=\!CH_2$$
$$|$$
$$CH_3$$
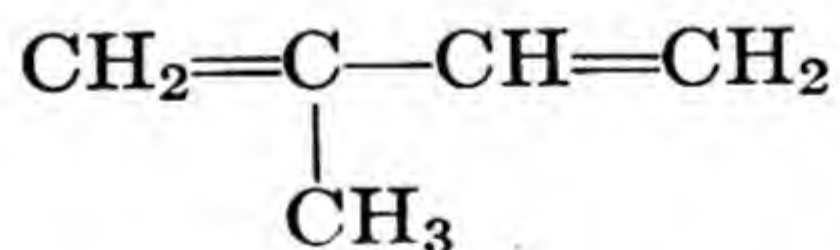
and the polymeric structure can be represented as

$$\left[-\!-CH_2\!-\!C\!=\!CH\!-\!CH_2\!-\!-\atop\qquad\quad |\atop\qquad\quad CH_3\right]_n$$
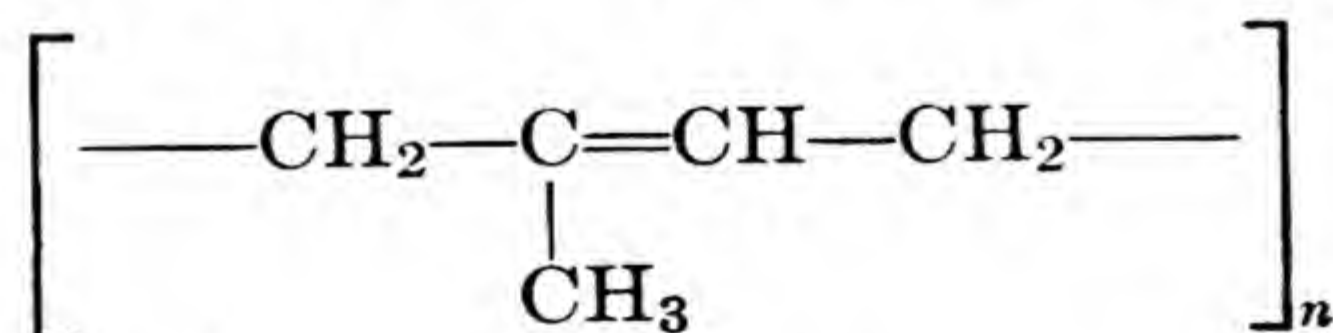
There is, however, the possibility of geometric isomers. The hydrocarbon obtained from rubber is assigned the *cis* structure, while that

221

obtained from balata and gutta-percha is believed to be *trans*. The following formulas represent the two isomers:
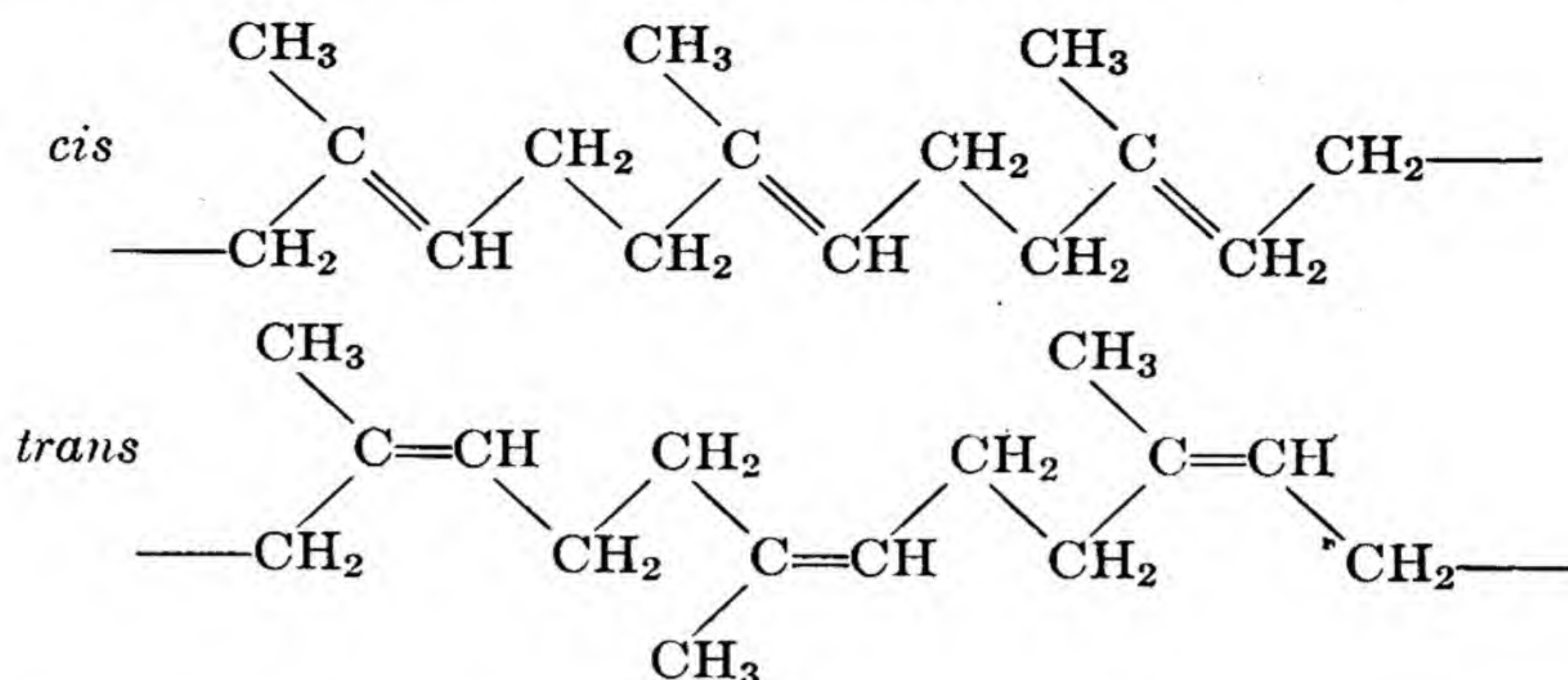
The latex is obtained by cutting a groove spirally around the tree and collecting the exudation in a cup hung at the lower end of the groove. The average annual yield from an acre of trees is approximately 500 lb. of dry rubber.

The latex is coagulated at the plantation by acetic or formic acid, and the slabs of coagulum are washed and squeezed between roller mills to remove the serum. The slabs are then dried either by air to produce crepe rubber or hung in smokehouses to prepare the grade known as "smoked sheets." In either form, the composition is about as follows:

Rubber hydrocarbon... 91.5%
Proteins.. 2.8%
Acetone soluble matter.. 2.9%
Esters insoluble in acetone... 1.0%
Water-soluble matter.. 1.0%
Moisture.. 0.5%
Ash... 0.4%

Several grades of this crude rubber are shipped to rubber plants for processing and molding. The first step involves working the rubber and mixing in all or part of a large variety of added materials, depending on the particular product being produced. Common addition agents are as follows:

1. *Reinforcing Agents.*—Certain fillers improve the tensile strength, abrasion resistance, and tear resistance of rubber. Channel carbon blacks and some clays are important fillers in this classification.

2. *Inert Fillers.*—These ingredients have little effect on strength or resistance but may improve processing properties or impart to the composition a desirable degree of hardness. Addition agents of this type include soft carbon blacks, barytes, whiting, slate flour, factice, etc.

3. *Plasticizers and Softeners.*—These materials are used to assist in mixing and processing rubber compounds. They act as lubricants in the mixture during the processing operations and accelerate the plasticization of the crude rubber. Softeners, chemical and mechanical, may also be used to modify the hardness of the finished product. This group includes resins, mineral and vegetable oils, waxes, and organic peptizing agents.

4. *Vulcanizing Ingredients.*—The various materials added for vulcanization are classed as follows:

   a. Vulcanizing agents. Sulfur, sulfur-bearing materials, or combinations of these with selenium or tellurium must be added for vulcanization.

   b. Accelerators. These materials reduce the time required for proper vulcanization or permit the use of lower vulcanizing temperatures, or both. They may be organic or inorganic materials.

   c. Activators. These compounds, both organic and inorganic, are used to supplement the accelerating effect of materials included in group *b* in order to secure some desirable characteristic in the finished product.

5. *Antioxidants.*—Various organic compounds are used to retard oxidation of the finished products and thus slow down deterioration due to exposure.

6. *Colors.*—Pigments and dyes are added to a compound to impart a desired color to the finished product. These ingredients may be inorganic pigments such as iron oxide, titanium oxide, or cadmium sulfide, or they may be organic dyes that produce brilliant colors when used in small amounts.

Mixing and Calendering.—The mixing of rubber is one of the most important steps in the manufacture of finished products. In this operation, the carefully weighed ingredients must be incorporated into the rubber in such a manner as to result in a perfect dispersion of each ingredient. The mixing operation is usually carried out on either of two types of equipment: a rubber mill or a Banbury mixer. The rubber mill consists of two oppositely revolving closely spaced smooth rolls, with one roll revolving at a slower speed than the other. The rolls are hollow, and cooling water is usually circulated through them to carry away the heat generated by the mechanical working of the rubber. The kneading action resulting from forcing the rubber through the small opening between the rolls plasticizes it so that a sheet is formed on the rolls which is cut and fed back to the top of the rolls. This process is continued until a homogeneous mixture is obtained.

The mixed compound is then formed into sheets, blocks, strips, or tubes by milling, extrusion, or calendering; or fabrics are coated by calendering or extrusion and built up into shapes. The various articles are vulcanized either in specially heated molds or by the application of heat alone.

Vulcanization.—The properties of crude rubber and vulcanized rubber differ considerably. Raw rubber is much inferior to vulcanized rubber both in elasticity and tensile strength. Under test conditions, raw rubber has a breaking strength of about 140 lb. per sq. in., while properly vulcanized rubbers show breaking strengths of the order of 2,800 to 4,200 lb. per sq. in. At low temperatures, the differences in breaking strength become less noticeable, and in both types almost all extensibility is lost. The elasticity of raw rubber is subject to changes with temperature to a far greater extent than vulcanized rubber. The latter maintains almost the same extensibility and strength over a wide temperature range, but raw rubber is satisfactory only over a relatively narrow temperature range. Crude rubber also exhibits complete recovery from extension only when the rates of extension and recovery are rapid; slow extension produces a high degree of permanent set. The rate at which vulcanized rubber is stretched exerts but little effect on its stress-strain properties.

The most important change occurring in rubber during the process of vulcanization is the great reduction of its plasticity while elasticity is maintained. The resulting product has greater strength and less surface tackiness. Accompanying these changes is an increased resistance to the swelling action of solvents. Properly vulcanized rubber differs from raw rubber in that swelling proceeds to a maximum and is not as a rule accompanied by passage of rubber into the solvent. This behavior is probably associated with the complex three-dimensional structure of the rubber agglomerate. Since swelling is the result of solvent molecules attempting to force the rubber chains apart into individual molecules, and vulcanization creates new bonds between rubber chains, it would be expected that vulcanized rubber would be attacked to a lesser extent by solvents. Not only the extent but also the rate of swelling is reduced by the vulcanization process.

Practically any process that increases the elasticity and tensile strength and reduces the tackiness of rubberlike materials has been termed "vulcanization." The story of Charles Goodyear accidentally dropping a mixture containing rubber and sulfur on a hot stove and then noting the remarkable change in the properties of the rubber has been well publicized as the actual beginning of the production of satisfactory rubber products. This development took place in 1839, and 17 years later the cold process using sulfur monochloride was discovered. Later on it was discovered that peroxides and polynitro compounds can produce the same effect.

There is no longer any doubt that the change in properties is brought about by an actual reaction between sulfur and the rubber hydrocarbon, but the exact nature of this reaction is still in doubt, at least in the processes requiring heat. It is beyond the scope of this work to discuss all the various possible reactions that might occur, but the following explanation presents the results attained.

The changes in plasticity and swelling are explained, provided an increase in the bonds between the hydrocarbon chains occurs. This change can be made one of degree, dependent on the extent of vulcanization, until hard rubber or ebonite is the final product. The purpose of a few cross linkages is to prevent slippage between chains and enhance extensibility. As these points of linkage become more numerous, the meshes between links become small and extensibility becomes less. Finally, a three-dimensional thermosetting structure is approached in the production of hard rubber. The production of crystallites may have an effect similar to actual cross linkages since the forces existing in the crystal lattice are powerful enough to have the same effect as actual chemical bonds.

The formation of crystallites accounts for several of the tensile properties of rubber. At high elongations stiffening occurs, and the stress-strain curve is concave toward the stress axis. Resistance to creep or plastic flow is increased. If the application of stress is slow and regular, rubber may be stretched without the appearance of crystallites, but the tensile strength of the stretched product is much less if crystallites are not formed. Upon the release of stress, the molecularly ordered state is unstable. Thermal agitation causes a breakdown of the crystallites and a return to the unordered amorphous structure possessing a more or less random arrangement.

If this is the true mechanism of what occurs, it requires that excessive slipping should not take place between chains. Many synthetic rubberlike materials do not form crystal lattices upon stretching. In these materials, many primary cross linkages between the long chains probably account for the absences of both slip and crystallites. In vulcanized rubber, enough primary cross linkages occur to cause greatly increased resistance to slipping of the long chains. In some cases, secondary valence forces, the so-called van der Waals' forces, between long chains may produce the same effect.

Much of the evidence to support these concepts of structure has been obtained by the use of X-ray diffraction patterns. The most widely accepted view of investigators in this field is that rubber may be pictured as a brush heap of entangled long-chain molecules. Early work by Katz revealed that the X-ray diffraction pattern for unstretched rubber consists of a broad halo, like that exhibited by liquids, which would be expected of the brush-heap structure. Elongation of rubber brings about a marked change in the pattern. Sharp diffraction spots appear. Such a pattern is typical of a system in which small crystallites exist. These ordered regions can be explained if, upon elongation following the application of stress, relatively short lengths of adjacent long-chain molecules become to some extent aligned and are close enough together so that they are then forced into a definite lattice, owing to the presence of sufficiently strong and regular intermolecular forces. One chain may extend both through

the crystal lattices and the surrounding amorphous regions. The difference between oriented and amorphous regions is similar to that pictured for cellulose on page 87.

The formation of crystallites has been observed in several synthetic rubberlike materials, particularly polyisobutylene and polychloroprene. Crystallites appear to form only where a uniform chemical structure is present in the long-chain molecules without an excessive number of primary valence cross linkages. Other synthetic rubberlike materials, notably the copolymers of butadiene, are always in the amorphous state. The cause for this appears to lie in the extensive cross linking between chains, as indicated by low solubilities in most solvents. Polymerization leads to the formation of chains of limited length, which then are linked to neighboring chains at one of the double bonds. The irregular structure thus formed precludes the possibility of the formation of a regular crystal lattice on stretching. In addition to cross linking, the introduction of a dissimilar monomeric molecule at irregular distances along the chain also leads to irregularity of structure and further reduces the possibility of crystallization.

The formation of crystallites is therefore not necessary for the production of rubberlike properties. Where crystallization does occur, similarities in structure are evident between rubber and synthetic rubberlike materials which are helpful in understanding the properties of the latter.

SYNTHETIC RUBBERS

Although natural rubber plantations had sufficient capacity to supply the world with rubber prior to the Second World War, the fact that 97 per cent of the rubber consumed by the United States was imported from the Far East caused this country to be entirely dependent on long marine transportation lines. The supply of natural rubber was cut off almost immediately on the outbreak of war and rapidly created an entirely different situation regarding synthetic rubber. The synthetic material almost overnight had to drop the role of a specialty product and assume the responsibility of eventually almost entirely replacing natural rubber.

If the atomic-bomb project is excluded, the wartime synthetic-rubber program was probably the greatest chemical engineering program ever attempted. This is certainly true if the comparison is limited to a like period of time. It would be a remarkable achievement even if it had been undertaken in relatively normal circumstances; as conditions existed, it was a stupendous undertaking. Admittedly there were periods when progress was unsatisfactory, and mistakes were made that are rather obvious in retrospect but were part of a very involved situation at the time.

The program was primarily directed toward the production of synthetic

rubber and the main essential ingredients for its manufacture. Monetary considerations were definitely secondary to obtaining a sure supply of synthetic rubber in the shortest possible time. It was rightly decided that the rubber situation was the most critical war-production problem and that a sufficient supply of synthetic rubber had to be maintained, regardless of costs or possible improvements in the processes and in the quality of
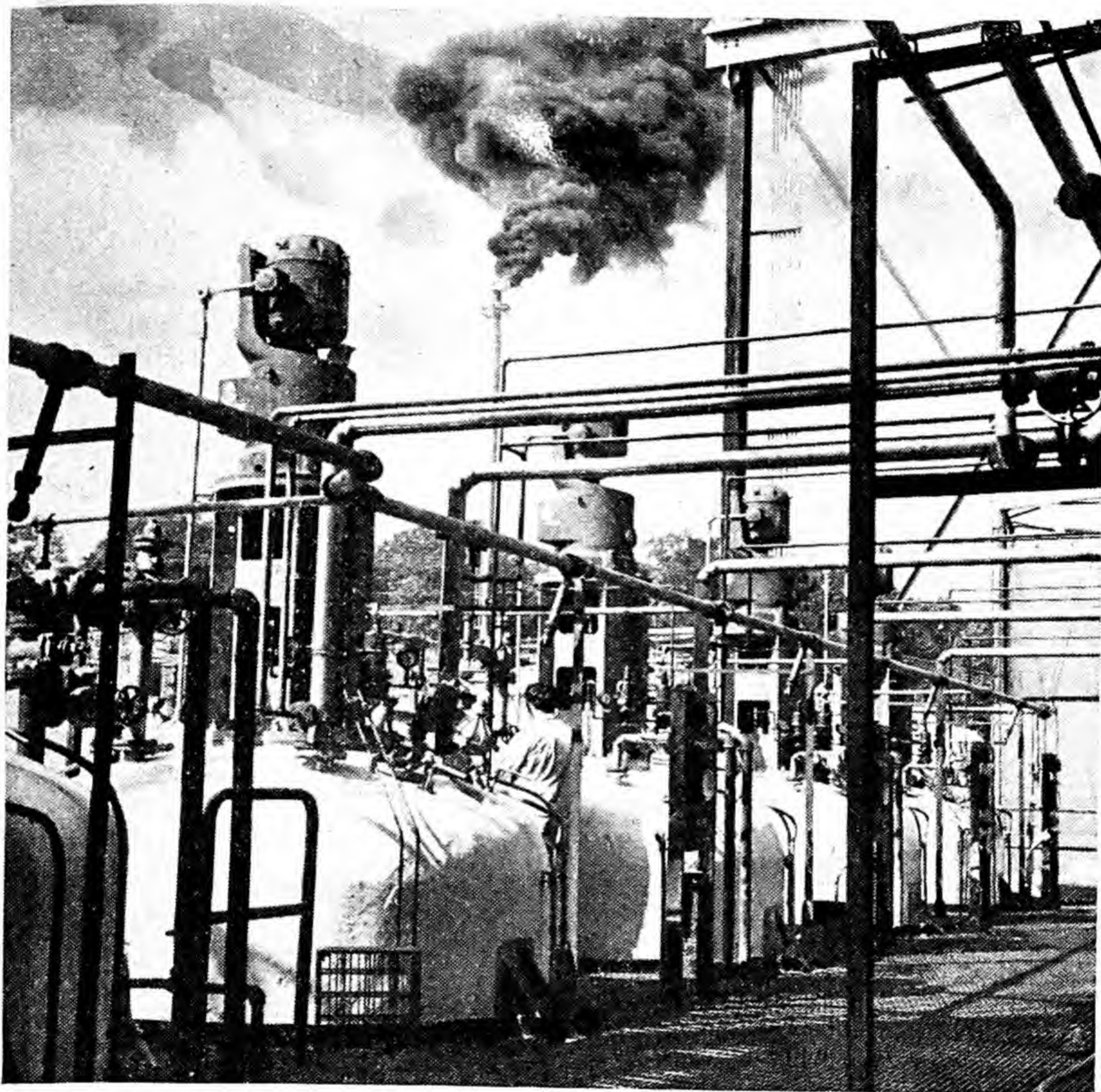
Fig. 105.—Reactors in a synthetic-rubber plant. (*Ewing Galloway photo.*)

product. Under these conditions, the job of getting out the rubber was undertaken by chemists and chemical engineers in many branches of the profession. With very little pilot-plant data, and in many instances without the physical properties of the materials being handled, plants were designed, built, and put into operation, very often faster than raw materials could be made available (see Fig. 105). The contribution of all concerned certainly was an important part of the war effort.

Table 6 shows the amount of synthetic rubber produced, together with the total rubber requirements for the years 1939 to 1945, and indicates the

required 5-year expansion of synthetic rubber from a minor industry producing 2,500 tons a year to a major industry producing a million tons each year.

TABLE 6.—PRODUCTION AND REQUIREMENTS OF RUBBER IN THE UNITED STATES

Year	Synthetic rubber production, tons per year	Total rubber requirements, tons per year
1939	2,500	800,000
1940	4,500	800,000
1941	9,000	800,000
1942	25,000	655,000
1943	235,000	545,000
1944	800,000	855,000
1945	1,000,000	1,100,000

The drop off in requirements during the years 1942 and 1943 was due to the strict civilian rationing program plus the fact that considerable time was required to reach total war-production capacities in all industries.

Considerable confusion regarding the type of synthetic rubber to be produced existed until the recommendations of the Baruch committee appeared in a report dated Sept. 10, 1942. Proposals had been made to obtain rubber from a great variety of growing plants or to produce synthetic rubber from every conceivable type of raw material. In the confusion, programs were started that could not yield rubber for 5 to 10 years. Russian dandelions, guayule, milkweed, and goldenrod were all planted or harvested, but the amount of natural rubber obtained from these sources was negligible.

The Baruch report[1] succeeded in channeling all efforts toward a fixed goal, although it had to be altered as developments occurred both in regard

TABLE 7.—CAPACITY IN TONS PER YEAR OF SYNTHETIC RUBBER PLANTS

Type of rubber	Baruch recommendations	Designed capacity	Ultimate capacity
GR-S..............	875,000	735,000	1,000,000
Butyl..............	139,000	75,000	75,000
Neoprene...........	69,000	63,000	70,000
Nitrile.............		30,000	30,000
Polysulfide.........		60,000	60,000

[1] BARUCH, B. M., J. B. CONANT, and K. T. COMPTON, 77th Congress, *House Doc.* 836 (1942).

to raw materials and technical experience with the early plants. Table 7 shows a comparison of the recommendations in the Baruch report, the designed capacity of the plants that were completed, and the ultimate capacity of those same plants.

Historical Development.—Early work on synthetic rubbers took place chiefly in Germany and Russia. In 1900, Kondakov reported that 2, 3-dimethyl-butadiene could be converted to an elastic mass, and the following year Thiele in Germany made a similar observation regarding 1-methyl-butadiene. It was not until 1910 that 1, 3-butadiene, the most generally used diene hydrocarbon at present, was shown by Lebedev[1] to give a rubberlike polymer, and the next year a similar result was reported by Harries[2] in Germany.

During the war interval 1914–1918, Germany is reported to have produced only about 2,300 tons of synthetic rubber, chiefly methyl rubber made from dimethyl butadiene derived from acetone. Three techniques of polymerization were used to give products designed for certain specific uses.[3] Mark H rubber, made by polymerization at room temperature for 3 or 4 months, was used for storage-battery boxes and tires and reached a maximum production rate of 40 to 50 tons a month. Mark W rubber, made by polymerization at about 160°F. (70°C.) for several days, was used for rubber-asbestos packings, insulated wire, balloon fabric, etc. Mark B rubber was made by metallic sodium-catalyzed polymerization in an atmosphere of carbon dioxide. This material had better working quality than did Mark H rubber and was superior for extruded shapes and insulation.

The importance of carbon black as a compounding ingredient for these synthetic rubbers was apparently not recognized, or the value of synthetic rubber to Germany during the First World War would probably have been far greater than it was. The postwar patent literature emanating from Germany stressed this importance of carbon black as a compounding ingredient.

Russian scientists also were actively engaged on a study of raw materials and polymerization processes for synthetic rubber. In 1915, Ostromislensky[4] showed how butadiene could be made by the pyrolysis of a mixture of alcohol and acetaldehyde. Ten years later Lebedev[5] modified the

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[1] LEBEDEV, S. V., *J. Russ. Phys.-Chem. Soc.*, **42**, 949 (1910); *Chem. Zentr.*, II, 1744 (1910).

[2] HARRIES, C. D., *Ann.*, **383**, 157 (1911).

[3] NORRIS, J. R., *J. Ind. Eng. Chem.*, **11**, 819 (1919); WHITBY, G. S., and M. KATZ, *Ind. Eng. Chem.*, **25**, 1204, 1333 (1933); BROOKS, B. T., *ibid.*, **34**, 799 (1942).

[4] OSTROMISLENSKY, I. I., *J. Russ. Phys.-Chem. Soc.*, **47**, 1472 (1915); SCHOTZ, S. P., "Synthetic Rubber," p. 49, Ernest Benn, Ltd., London, 1926.

[5] LEBEDEV, S. V., Fr. 665,917 (1928); *C.A.* 24, 1390 (1930); TALALAY, A., and L. TALALAY, *Rubber Chem. Tech.*, **15**, 403 (1942).

method and developed it into a commercial process for the U.S.S.R. The butadiene was polymerized with sodium to a synthetic rubber known as SKB, the letters standing for the Russian words for synthetic rubber made by process B from alcohol. Large-scale production was in progress in 1932, and by 1937 it was reported that the capacity was about 90,000 tons annually.[1]

Efforts to produce synthetic rubber in Germany were continued, and in 1934 the buna rubbers were developed from butadiene as a base. Commercial production began in 1935 under a protective government tax on crude-rubber imports. Apparently the German government dominated the research and production of synthetic rubber by 1935.

The three grades of buna first produced by the sodium polymerization of butadiene alone (bunas 32, 85, and 115) were inferior to those made by the special copolymerization of butadiene with styrene, buna S, and with acrylonitrile, buna N and NN. The acrylonitrile copolymers were the only ones exported from Germany to the United States.

In Russia, the first tires with 100 per cent sodium–butadiene rubber, SK rubber, treads and side walls were made in December, 1932, at the Krasnaya Treugolnik,[2] and soon rubber factories at Leningrad and Jaroslaw were working on similar lines. Russia also produced Sovprene, the Russian variety of neoprene.

In the United States, synthetic rubber had been developed for special-purpose uses, but the synthetics were unable to compete with natural rubber in those instances where the natural product was satisfactory. Production of these synthetics, especially the oil-resistant forms, grew from about 2,500 tons in 1939 to 9,000 tons in 1941, and then was tremendously accelerated as a war measure.

Polysulfide rubber (thiokol) was accidentally discovered in 1923 by J. C. Patrick while he was working on antifreeze compositions. He noted the rubberlike properties of the reaction product and obtained patents in 1928. A company was organized, and commercial production of this oil-resistant specialty rubber was begun in 1929.

In contrast to this accidental discovery, a definite research program leading to the development of a chemically resistant synthetic rubber was undertaken by one of the large chemical research laboratories. Work got under way in 1925, and a few years later it was decided to concentrate on the development of polychloroprene. This project resulted in the commercial production of polychloroprene rubber, called Neoprene, in 1931.

Butyl rubber was developed in the latter part of the 1930's and had reached the pilot-plant stage by 1940. A large-scale commercial plant was started in 1941, but ensuing production difficulties in large-scale operation prevented the marketing of appreciable amounts until 1943.

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[1] TALALAY, A., and L. TALALAY, *Rubber Chem. Tech.*, **15**, 403 (192).
[2] *India Rubber World*, **106**, 76–79 (1942).

Several companies in this country were experimenting with the acrylonitrile-butadiene copolymer in the late 1930's, and several relatively small commercial units were in operation by 1941.

These four rubbers were the only ones that had reached some stage of commercial development at the outbreak of the war. It is interesting to note that the butadiene-styrene copolymer, GR-S, was not one of the four, yet the entire rubber program eventually centered around it. Although several laboratories were familiar with butadiene-styrene copolymers, their experience did not extend far beyond the glassware stage. In spite of the lack of experience with GR-S, it was chosen because of the raw-material situation, since the eventual large-scale production of butadiene and styrene would interfere less with the existing "chemical balance" during the war than would a sudden increase in demand for raw materials for any of the other satisfactory rubbers.

Commercial Synthetic Rubbers.—Out of these earlier developments evolved the five principal types of synthetic rubbers now in production.

GR-S
$$\left[(-CH_2-CH=CH-CH_2-)_x-\underset{\underset{C_6H_5}{|}}{CH}-CH_2- \right]_n$$

Nitrile rubber (GR-A)
$$\left[(-CH_2-CH=CH-CH_2-)_x-\underset{\underset{CN}{|}}{CH}-CH_2- \right]_n$$

Butyl (GR-I)
$$\left[-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}- \right]_n$$

Neoprene (GR-M)
$$\left[-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2- \right]_n$$

Polysulfide rubber (several types)
$$\left[-CH_2-CH_2-\underset{\underset{S}{\|}}{S}-\underset{\underset{S}{\|}}{S}- \right]_n$$
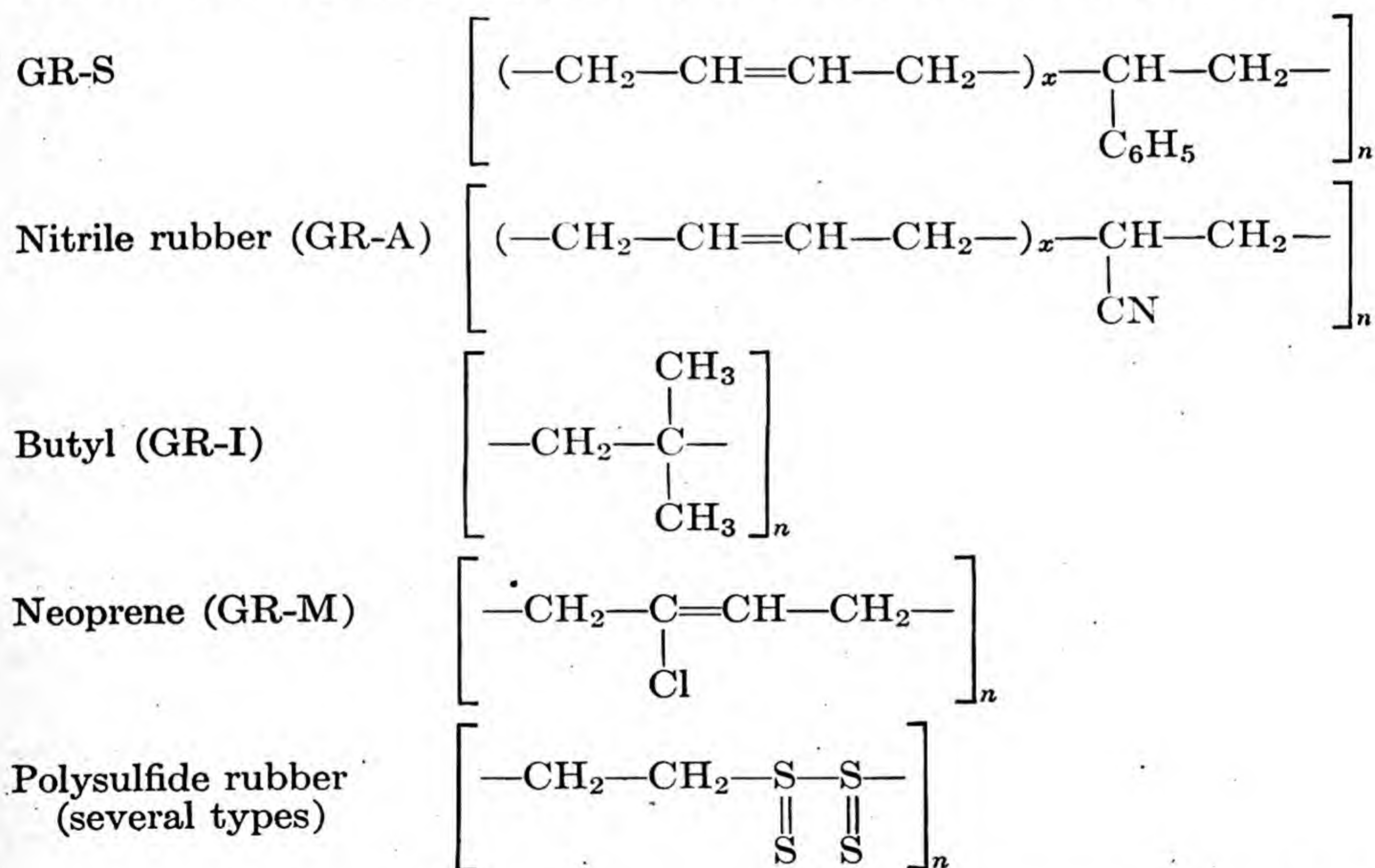
In some respects this classification of synthetic rubbers can be considered to be incomplete since it does not include several rubberlike resins that can be used as rubber substitutes for many purposes; in fact, in most of their applications they are more than rubber substitutes since their performance is far superior to rubber. Polyesters, vinyl polymers, and copolymers and polystyrene are all resins of this type but are better classified under their respective types since their rubberlike character is chiefly one of degree rather than a principal property, and they have all been

discussed under their respective classifications. The definition of a rubber must be based on consideration of its performance at, or close to, room temperature and can include many borderline products such as the polyesters.

A rubber is defined as a product that can be stretched to at least double its original length and is then capable of retracting rapidly and forcibly to substantially its original dimensions. To be useful it must exist in a raw plastic state that can subsequently be vulcanized, causing the article to retain its shape and dimensions. The requirement of vulcanization limits the commercial synthetic rubbers to the five types in the classification with the exception of some of the polyesters that have been included along with the chemically similar resins in class II.

The vulcanization of synthetic rubbers produces an effect similar to the vulcanization of natural rubber, but the actual process may differ considerably. Sulfur is not necessarily the vulcanizing agent but usually has an effect on the process. Chloroprene polymers can be vulcanized with magnesium oxide without the use of sulfur. In this case, the reaction that forms the cross linkages occurs between the magnesium oxide and two chlorine atoms. Various degrees of vulcanization may be obtained, depending on how far the reaction is carried but it is not possible to form a "hard" product. Other synthetics are vulcanized by sulfur and rubber accelerators to form the same range of products that are produced with natural rubber.

All the synthetics in this classification will undergo vulcanization but may not require it for many applications. The cycle of rubber processing is important in the evaluation of synthetic rubbers. When natural rubber is worked on rolls, it is plasticized or depolymerized to some degree. This makes it much easier to work in the later stages of processing. This breakdown of the hydrocarbon chains has the same effect as the addition of plasticizers, but there is a marked advantage in that the effect on the material being processed may easily be removed by vulcanization—in fact the curing process is usually carried beyond the equivalent of raw rubber. If chemical plasticizers or softeners are required for processing, it is usually difficult to remove them or to counteract their effect. Many of the problems encountered with various synthetic rubbers are related to the ease with which they undergo plasticization by working and vulcanization.

Theoretically, a suitable synthetic rubber would be a linear hydrocarbon polymer of the right consistency for processing, or easily degraded to the proper consistency, which had the proper amount of chemically reactive groups so that the desired degree of cross linkage could be produced by vulcanization after molding. However, it should not contain highly polar groups that would cause too great an attraction between the chains and destroy the rubberlike properties. In addition, the number of reactive groups should not be much greater than those required to produce cross

links, particularly if stability and chemical resistance are desired. Butyl rubber was based on this concept. The amount of residual unsaturation introduced is proportional to the degree of vulcanizability desired. It should be realized that this concept of rubberlike structure and properties is certainly not the whole story. Molecular weight distribution, thermodynamic and physical properties are also extremely important and may be the controlling factors for a particular application.

The whole problem is more complicated when synthetics are considered because the polymerization reaction does not always tend to produce linear polymers. Branching of the chains frequently occurs as well as cross linkage. Unless this tendency is controlled, a product is obtained that is already the equivalent of being partially vulcanized and is much more difficult to process. This is what occurs in the polymerization of most synthetics. They then require more severe working or plasticizers, or both, resulting in a corresponding decrease in some of the physical properties of the finished product.

A rubberlike consistency can be obtained with many synthetic resins by the incorporation of considerable amounts of plasticizers and some control over the average molecular weights. These materials, such as plasticized polyvinyl chloride, are excellent substitutes for rubber in many applications and are far superior to rubber and most synthetic rubbers under certain conditions. However, most of their rubbery properties are due to the effect of the plasticizer and not to their molecular structure.

A detailed discussion of the methods of production and the properties of the various synthetic rubbers is included in the following pages.

GR-S.—Copolymers of butadiene and styrene know as buna S or GR-S are by far the most important synthetic rubbers at the present time. Butadiene and styrene are copolymerized by emulsion polymerization in approximately a 3:1 ratio by weight. In commercial practice, neither raw material is pure, since some of the monomers are recovered from the polymerized material and recycled. The recovered monomers usually contain small amounts of partly polymerized material. The relative proportions of the various materials charged to the reactor are approximately as follows:

	Parts by Weight
Butadiene	75.0
Styrene	25.0
Soap (solid)	5.0
Water	180.0
Modifier	0.5
Catalyst	0.3
Total	285.8
Stabilizer (added at end of polymerization)	1.6
Total	287.4

The hydrocarbons are added to a solution of soap in water in the polymerizer and are emulsified by agitation. A small quantity of an organic modifier is added to improve the properties of the finished polymer, partly, at least, by reducing cross linkage. A small amount of a catalyst such as potassium persulfate serves to increase the rate of reaction. The butadiene, styrene, and soap solution are passed through liquid-displacement meters, while the catalyst and other materials are measured in weigh tanks. All except the catalyst pass through a common header in order to prevent charging the several materials in layers. Conditions of reaction are controlled by means of a group of temperature- and pressure-recording controlling devices.

The reactors are water-jacketed, glass-lined, or stainless-steel kettles with agitators. They are provided with hot- and cold-water circulating systems for the exact control of reaction temperature. In some plants, stainless-steel coils inside the vessel are also provided. In order to seal the volatile butadiene against loss from stuffing boxes, a special Dura-metallic seal is used which operates on the principle of sliding metallic rings, working under a positive oil pressure to prevent the loss of volatile material. Each reactor is provided with a combination frangible disk and a spring-tension type of pressure relief valve discharging through a collector system of pipes to a safety flare.

The reaction mass is brought to the polymerization temperature of 50°C., and the reaction is continued for about 13 hr., or until the conversion of the monomers to copolymer is about 80 per cent completed. When this conversion is reached, the latex in the reactor is blown down by its own pressure to blowdown tanks in which the polymerization reaction is arrested by addition of stabilizers known as "shortstops." Each one of these tanks is large enough to hold the contents of three reactors. From this point on, the process becomes continuous. The latex is pumped to flash tanks in which the pressure is reduced in two stages and the excess butadiene vented off. The unreacted styrene is recovered in stripping towers by blowing with steam. Both recovered monomers are returned to the process as raw materials.

The latex, free from butadiene and styrene, is conveyed by diaphragm pumps to several 30,000-gal. concrete blending vats, where the various batches are mixed to produce a uniform product. The antioxidants are added in the line by means of proportioning pumps as the latex enters the vat.

From the blending vats the latex is pumped to a wooden creaming tank where brine is added to flocculate the rubber particles. Next it goes to the coagulation tank and the soap-conversion tank where acid is added and the soap is converted to fatty acid. The mass is transferred by Duriron pumps to the riffler box above a rotary filter equipped with

squeeze-press rolls. The mass as it reaches the filter contains about 5 per cent solid rubber (see Fig. 106). The dilute acid solution is first removed and stored for reuse. The rubber crumbs are then washed free of acid
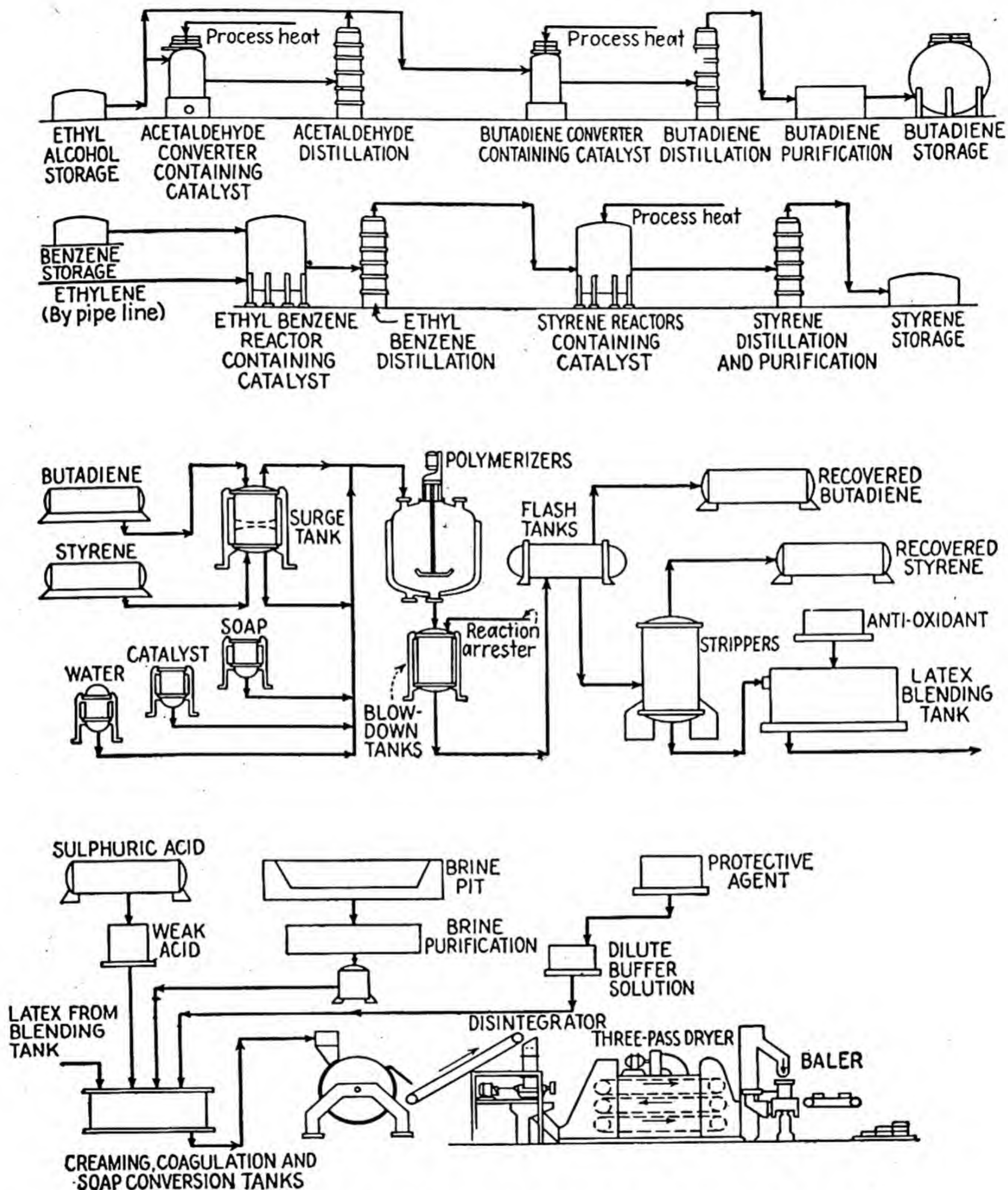
FIG. 106.—Flow sheet for GR-S rubber. (*Chem. and Met.*)

and conveyed by a rubber belt to a large disintegrator. After being broken up, they drop to a tunnel drier and are conveyed the length of the drier three times. The product is fed to the top belt and transferred progressively to the second and third belts for complete drying. The drier

discharges onto a screw conveyer which feeds the scales. An automatic baler compresses it into 75-lb. blocks and places them in cardboard containers for storage and shipping. The bales of GR-S are shipped to rubber factories for processing into finished articles on the same machinery and by processes similar to those employed for natural rubber.

The rock salt is delivered to the plant in freight cars and dumped into underground concrete storage pits. The salt is flooded with water to prepare a saturated brine. The brine is pumped to a purification system to remove the calcium and magnesium in the brine. Both of these impurities would eventually be precipitates in the synthetic rubber as salts of fatty acids and would interfere with the curing properties in tire-building operations.

The structure of butadiene polymers and copolymers has an important bearing on the properties of finished articles produced from them. The control of the course of the polymerization reaction to produce the desired structure is one of the important goals of a considerable amount of research.

Butadiene can polymerize so that either 1, 4 or 1, 2 addition takes place. If 1, 4 addition was the only mechanism, a straight-chain polymer would be produced containing the same arrangement of double bonds as natural rubber.

$$—CH_2—CH=CH—CH_2—CH_2—CH=CH—CH_2—$$
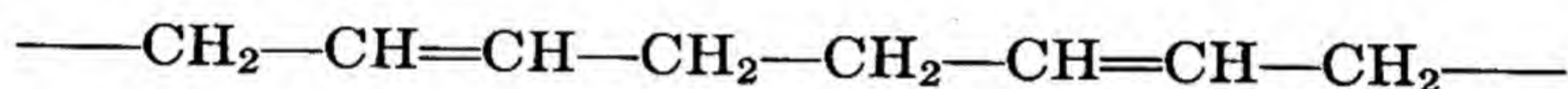
If the reaction were exclusively 1, 2 addition, a typical saturated polyethenic chain with vinyl groups substituted on alternate carbon atoms would be produced.

$$
\begin{array}{c}
—CH_2—CH—CH_2—CH— \\
\quad\quad | \quad\quad\quad\quad\quad | \\
\quad\quad CH \quad\quad\quad\quad CH \\
\quad\quad \| \quad\quad\quad\quad\quad \| \\
\quad\quad CH_2 \quad\quad\quad\quad CH_2
\end{array}
$$
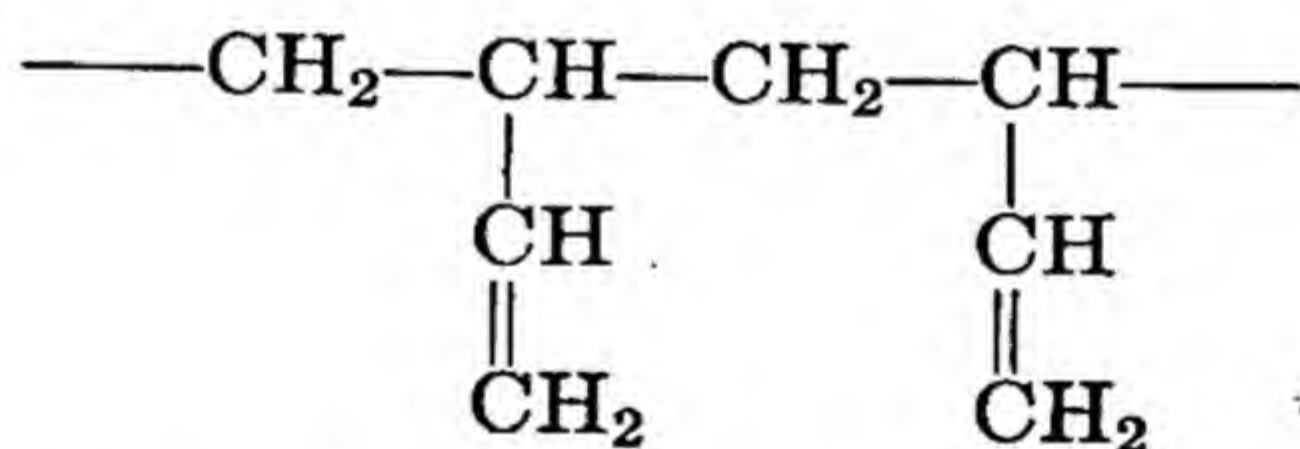
It is well established that the 1, 4 addition predominates, but there is good evidence that some 1, 2 addition takes place. This would produce occasional branching or cross linkages as follows:

$$
\begin{array}{c}
—CH_2—CH=CH—CH_2—CH_2—CH—CH_2—CH=CH—CH_2— \\
\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad —CH \\
\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad\quad\quad\quad\quad\quad CH_2—CH_2—CH=CH—CH_2—
\end{array}
$$
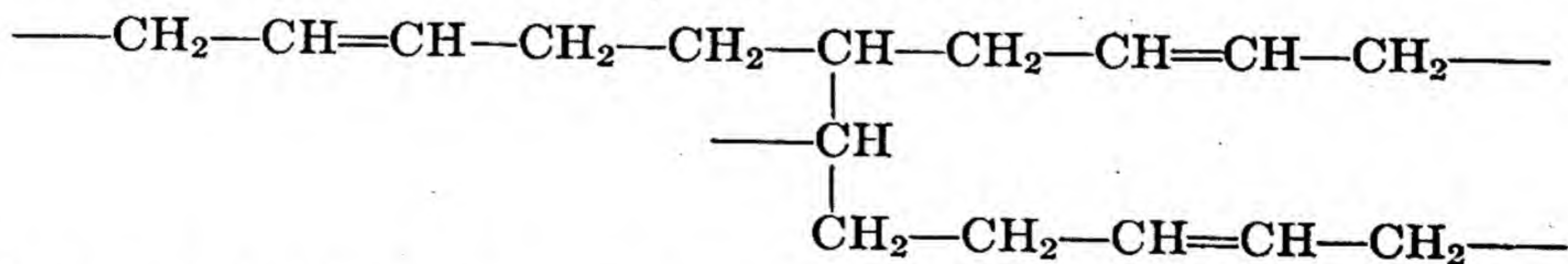
The exact structure produced would depend on many factors such as relative rates of chain growth, relative effect of cessation reactions, and the actual structure of the end groups. Modifiers are added to the reactants in attempts to reduce the amount of branching and cross linkage. These modifiers might be classed as directive catalysts since their function is to

direct the reaction toward the formation of linear polymers. It should be remembered that the degree of polymerization also has an important effect on the properties of the polymer as well as on the actual structure. However, mastication probably has a greater effect on the degree of polymerization than it does on the structure.

So far the effect of the copolymer has not been mentioned. It was discovered that the introduction of styrene or acrylonitrile gave a copolymer, which, although much more difficult to process than natural rubber, was far superior to straight polybutadiene in this respect. The introduction of styrene into the structure produces occasional irregularity that complicates the picture considerably by adding many more possible variations. This irregularity, together with the rather frequent branching or cross linkages, is probably the reason GR-S does not give a crystallite X-ray diffraction pattern when stretched.

The butadiene and styrene are originally present in about a 6:1 molar ratio, yet the product has 7 to 7.5 butadiene units to each styrene group. Thus the rate at which they tend to polymerize is not the same and may change during the course of the reaction.

GR-S requires more severe milling than natural rubber, but overmilling causes a considerable decrease in the tensile strength of the product so that mastication must be closely controlled. Larger quantities of plasticizers and softener are also required. The vulcanization reaction does not require as much sulfur but greater amounts of accelerators must be used. Curing agents, fillers, and activators are similar to natural rubber. The reinforcing action of carbon black is much more pronounced, particularly when comparatively large amounts are used. The type of carbon black added for specific uses is also very important. Special carbon blacks have been developed for reinforcing GR-S.

GR-S is definitely superior to natural rubber in resistance to aging and has a lower permeability to gases. There is not a great deal of difference in tensile strength, resilience, elasticity, and abrasion resistance. The chief disadvantages of this type of synthetic are its low resistance to tear, high heat generation, inferior rebound, and the greater difficulty of processing. Despite these deficiencies, it was chosen as the best general-purpose rubber for the emergency wartime synthetic-rubber program and became the main substitute for the natural product. In 1945, there was an estimated annual plant capacity of 1,000,000 tons for GR-S production in the United States and Canada. A recently developed continuous polymerization process has been operated on a commercial scale. Continuous operation of the polymerization step would make it possible readily to increase plant production above the estimated 1,000,000-ton capacity.

This synthetic is a general-purpose rubber, and its applications include almost the entire range of rubber products. It should not, however, be

used where extreme temperature conditions are encountered or in the presence of oils, solvents, or chemicals in general.

Nitrile Rubber.—Nitrile rubber is a copolymer of butadiene and acrylonitrile. The ratio of butadiene to acrylonitrile is approximately the same as the ratio of butadiene to styrene in GR-S, and the method of obtaining the raw rubber is almost identical to the GR-S process. For this reason, a detailed description will not be given. An intensive development of continuous polymerization processes for making this product is also under way at present.

Because of the fact that this synthetic rubber does not break down so easily as natural rubber, the use of softeners is important. Softeners of the ester type (phthalates) are most effective as well as wool grease and pine and coal tars. The sulfur content that is necessary to induce good vulcanization can be lower than for natural rubber. The tensile strength of a vulcanized unpigmented nitrile stock is only a fraction of that of a corresponding natural rubber compound, but it can be raised to a value closely approaching high-grade natural products by the incorporation of special grades of carbon black. As was true for GR-S, carbon black has a remarkable effect of increasing the tensile strength of compounds made from this copolymer. Other fillers impart a high degree of reinforcement, but the effect is not nearly so pronounced as that produced by carbon black.

Nitrile rubber compounds can be made to compare favorably with natural rubber as far as tensile strength, elongation, and abrasion resistance are concerned. They are definitely superior to both natural rubber and GR-S wherever resistance to oils, solvents, or chemical reagents is concerned, although in some cases this chemical resistance is exceeded by that of some of the other synthetic rubbers. However, a comparison of one specific property without taking into consideration many others may be very misleading. Thus chemical resistance in a specific compound might be gained at the expense of elasticity. If good elasticity was required, it obviously could not be sacrificed for improved resistance to chemical attack. A relative comparison of all the properties of the various rubbers is given in Table 8 in the Appendix.

Products made from nitrile rubber are definitely inferior to natural rubber in adhesion and tear resistance. They also have a slightly greater gravity, which may be detrimental in some applications.

The properties of this synthetic make it extremely useful in the manufacture of carburetor diaphragms, self-sealing fuel tanks, aircraft hose, and gaskets. It is also employed in the fabrication of gasoline hose for service-station pumps, large-size hose for handling oil, and for cables that must resist oils and abrasion. It is used in molded articles, especially mountings for machinery and shoe soles for service where oils are present. Printing rolls, blankets, and plates are additional applications.

Isobutene-Diolefin Copolymers.—These copolymers, generally known as butyl rubber, are designated in government terminology as GR-I. They were discovered as the result of an attempt to "design" a synthetic rubber by introducing a small amount (about 2 per cent) of a diolefin to provide unsaturation for vulcanization. The product therefore has low unsaturation, with an iodine number of 1 to 2 per cent of that found in natural rubber. The raw product resembles natural rubber in appearance, except
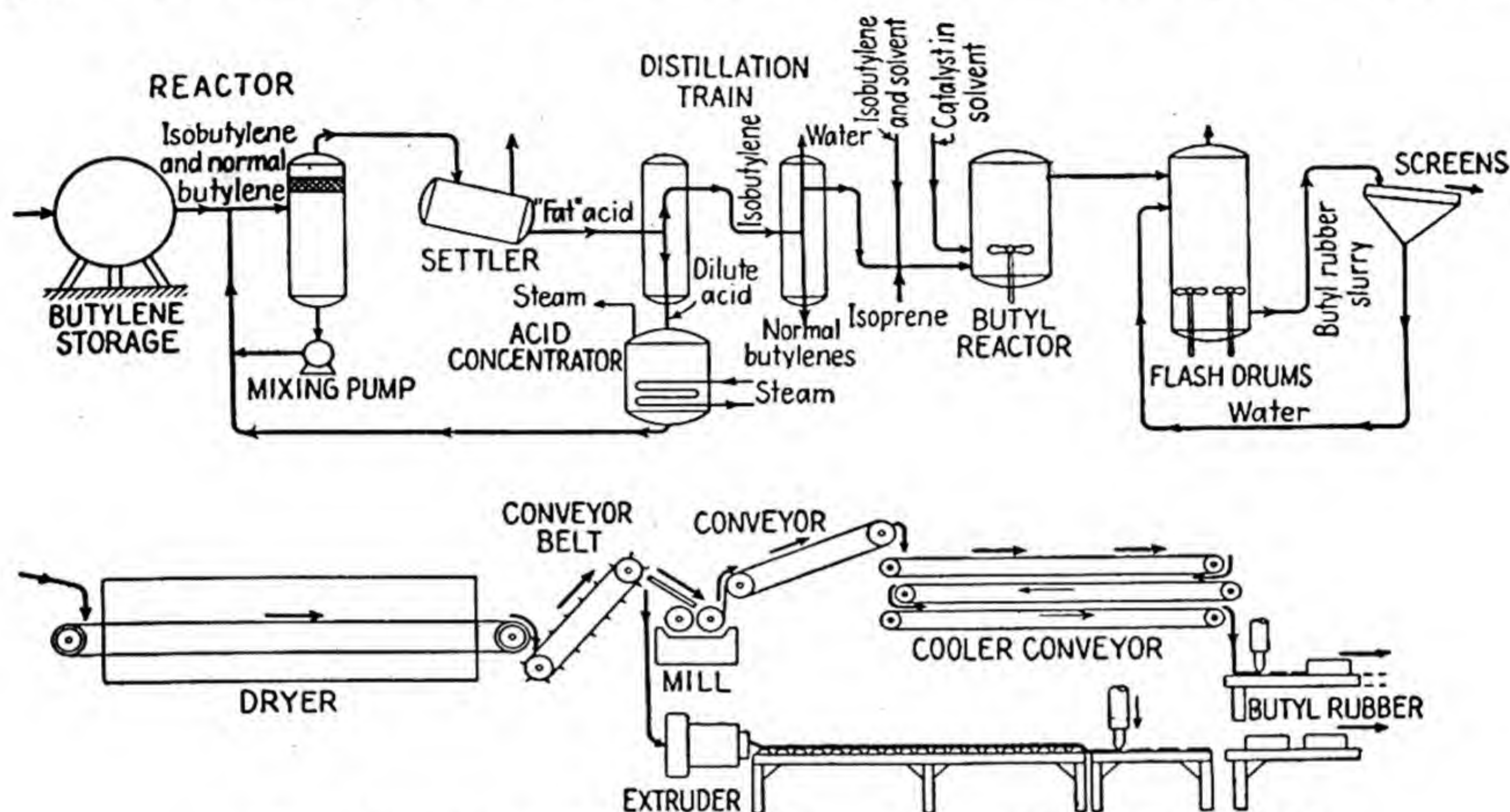
FIG. 107.—Flow sheet for butyl rubber. (*Chem. and Met.*)

that it is colorless and odorless. The molecular weight of the finished product ranges from 40,000 to 80,000, and it has density of 0.91.

Isoprene is usually the diolefin that furnishes the unsaturation. Most of the isoprene now used is produced in the naval-stores industry, but it may be made from petroleum. Gases produced in various petroleum-cracking operations contain the C_4 fractions that are used as raw materials for isobutene production. The butenes are subjected to an extraction process for removal of butadiene, leaving a mixture of butenes and isobutenes. This mixture is sent to another plant where isobutene is extracted for subsequent use in the production of butyl rubber. The process is shown diagrammatically on the flow sheet (Fig. 107). The remaining butene is sent to the dehydrogenation plant where it is converted into additional butadiene. At the butyl plant the isobutylene extraction is subjected to a redistillation to remove traces of moisture and any undesirable fraction. It is then ready for utilization in the polymerization reaction.

The isoprene contains an inhibitor that is removed by distillation immediately prior to its use. Isobutylene and isoprene are mixed together with a diluent in mixing tanks and then fed continually to a reactor. This feed stream is chilled to a temperature of −150°F., using both ammonia

and ethylene for refrigeration before entering the reactor. A catalyst is introduced into the bottom of the reactor.

The reaction is carried out at approximately −150°F. Sufficient agitation is provided to maintain a thin slurry. The amount of catalyst introduced is controlled to give the desired conversion of isobutylene to butyl rubber.

The products of this reaction, which include the polymer, unreacted isobutylene, and diluent, flow into a flash drum maintained at +150°F. This temperature is sufficient to vaporize the unreacted isobutylene and the diluent and also to destroy any catalyst that may remain. The slurry is then passed through a stripper, operated under vaccum to remove the last traces of the diluent. Part of the water is removed by a vibrating screen, and the butyl crumbs are dried in a tunnel drier at 150 to 220°F. Material leaving the drier is either extruded or milled. In both methods of operation, a ribbon of rubber is produced that passes through a long series of conveyers where it is cooled by a current of air passing over it. This ribbon is then cut into sheets and boxed for shipment.

The isobutylene and diluent from the flash drum are compressed to 30 lb. pressure, dried in alumina driers, further compressed to 200 lb. pressure, and separated in a series of fractionating towers. Some of the constituents are recycled back to the reactor feed drums, and others are discarded from the system to prevent accumulations of undesirable materials in the polymerization section.

The rubber is shipped in the uncured condition and contains 1 part by weight of zinc stearate and one-half part by weight of phenyl beta naphthylamine. It is tacky and has a tendency to flow under its own weight and to adhere to storage racks. It does not require mastication before being compounded; so the compounds can be mixed effectively in a Banbury mixer.

The compounding of this material is similar to that of natural rubber except that more vigorous vulcanizing agents are required. Small amounts of softeners are all that are required. Vulcanization is carried out at higher temperatures than those ordinarily used for natural rubber in order to obtain curing times that approach those of the natural product.

Since these copolymers contain very little residual unsaturation, they are chemically inert and are superior to natural rubber for many purposes. They are used for laboratory tubing and electrical insulation, for the manufacture of gas masks and clothing to resist chemicals and war gases. Butyl is much more impermeable to the passage of gases and much more resistant to sunlight and aging. These properties make it particularly applicable for such articles as pontoons, life rafts, and rubber life jackets. Since it is soluble in paraffinic hydrocarbons, toxic aromatic solvents are not required in rubber cements made with butyl.

Butyl is particularly adaptable to the manufacture of inner tubes. Inner tubes may be made from it almost as easily as they can be made from natural rubber. The tubes are very serviceable owing to their ability to prevent the diffusion of air and their very excellent tear-resisting properties.

As might be expected from the low degree of unsaturation, the age resistance of the vulcanized rubber is excellent, and it is unnecessary to add antioxidants. Strong sulfuric and nitric acid leave it intact, even after days of immersion, and it is resistant to most other chemicals. At room temperatures the vulcanized synthetic rubber has a very low rebound, but at temperatures approximating 100°C. balls of this material give approximately the same bounce as those made from natural rubber. Recent developments in compounding have indicated that, by the addition of proper plasticizers or softeners, a higher degree of resiliency at room temperature can be imparted to these copolymers. Like natural rubber, the material swells in petroleum and coal-tar solvents but not in most vegetable and animal fats. Hydrogen and nitrogen diffuse through it at about one-tenth the rate of passage through natural rubber. Its water absorption is about one-fourth that of natural rubber.

Butyl has a consistency equivalent to that of moderately broken-down natural rubber, and it is therefore ready for incorporation of pigments and other agents. In contrast to GR-S and nitrile rubber, additions of carbon black increase the resistance to abrasion but cause a decrease in tensile strength. Compounds of butyl rubber are not adapted for tire treads, even though they have high resistance to flexing both when freshly compounded and after long aging.

Polychloroprene.—Polychloroprene is produced from acetylene and hydrochloric acid by a series of reactions. If acetylene is treated with cuprous chloride, dimerization to vinylacetylene occurs.

$$2HC\equiv CH \xrightarrow{Cu_2Cl_2} H_2C\!=\!CH\!-\!C\equiv CH$$
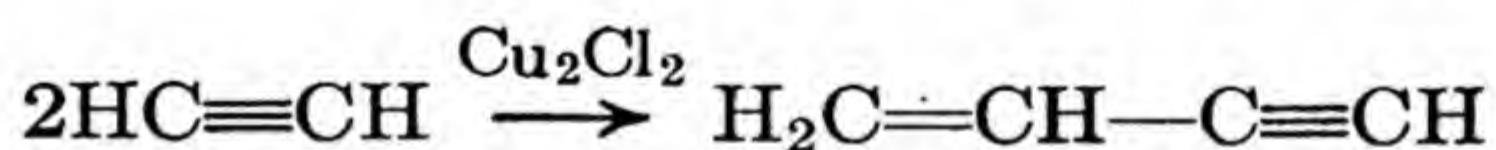
Some divinylacetylene is formed in this reaction and represents a by-product for which no practical outlet has been devised. The amount of divinylacetylene formed is kept at a minimum, and that formed is removed by distillation. The purified vinylacetylene is then treated with hydrogen chloride in the presence of both cuprous chloride and ammonium chloride to give an unstable isomer of chloroprene by 1,4 addition.

$$CH_2\!=\!CH\!-\!C\equiv CH + HCl \xrightarrow[NH_4Cl]{Cu_2Cl_2} ClCH_2\!-\!CH\!=\!C\!=\!CH_2$$
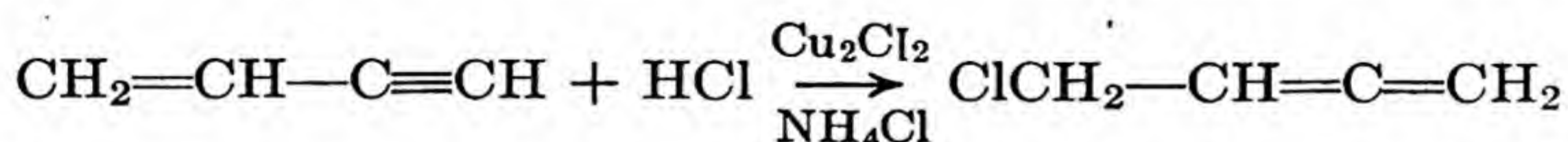
Since this chloride is of the allyl chloride type, 1,3 rearrangement to 2-chlorobutadiene under the catalytic action of hydrochloric acid occurs.

$$ClCH_2\!-\!CH\!=\!C\!=\!CH_2 \xrightarrow{\text{HCl}} CH_2\!=\!\underset{\underset{Cl}{|}}{C}\!-\!CH\!=\!CH_2$$
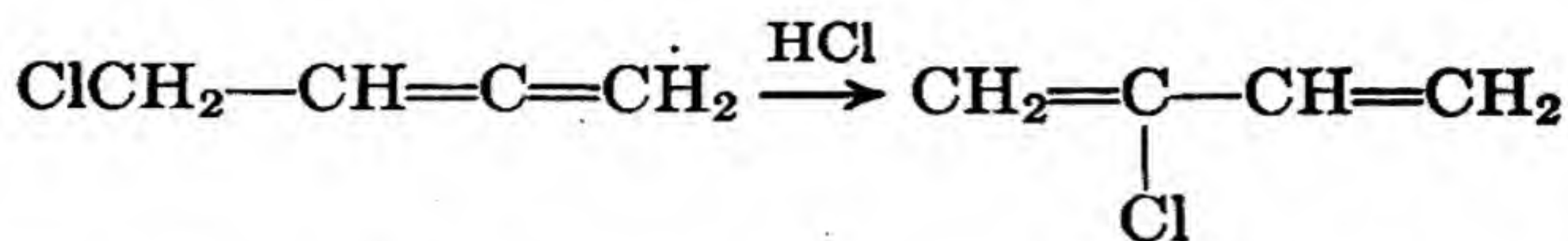
The chloroprene is then polymerized in the presence of a suitable catalyst to polychloroprene, usually called "neoprene."

$$CH_2\!=\!\underset{\underset{Cl}{|}}{C}\!-\!CH\!=\!CH_2 \longrightarrow \left[-\!-\!CH_2\!-\!\underset{\underset{Cl}{|}}{C}\!=\!CH\!-\!CH_2\!-\!- \right]_n$$
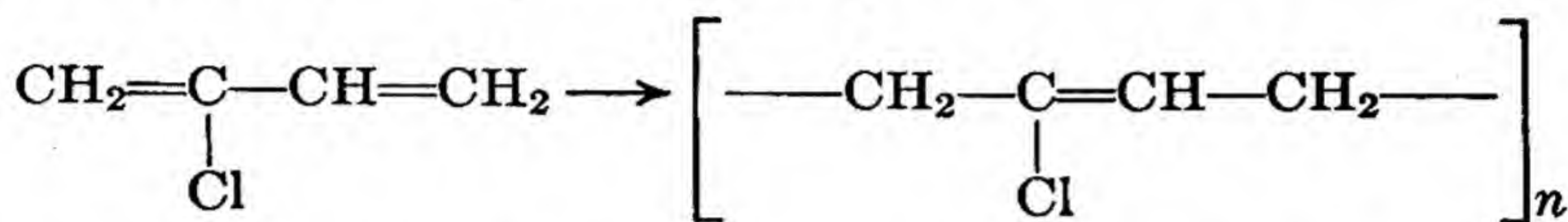
Polychloroprene is manufactured commercially on a large scale by emulsion polymerization. Emulsions are formed with the aid of soaps or amino wetting agents in aqueous solutions. Emulsion polymerization has made possible the production of newer types of polychloroprene as well as copolymers of chloroprene with other monomeric substances. During the polymerization some hydrochloric acid is liberated. In order to prevent the coagulation of the latex in the presence of the acid, ammonium hydroxide is added to the emulsion. Coagulation of the resulting latex is usually effected with acetone or some other organic liquid that can be easily recovered (see Fig. 108).

After coagulation and drying, a small amount of a stabilizing material, such as phenyl-β-naphthylamine or tetramethyl thiuram disulfide, is added to prevent further polymerization. Softeners are also added to improve the milling properties of polychloroprene. Plasticizers are required for most stocks. The most frequently used plasticizers are the phthalates and various oils. Originally, polychloroprene did not masticate well on rubber mills, and considerable difficulty was experienced in processing.· More recent types, however, much more closely resemble natural rubber in that they can be plasticized by working. In the production of this type of polychloroprene, a continuous process is used with close temperature control. The polymer is removed from the emulsion by coagulation on a rotating chilled drum, and the film that forms is continuously sheared off in the form of a belt, washed with water or other liquid, and passed through a drying oven (see Fig. 109). The material is brought to the proper degree of plasticity by milling under water or with chemical plasticizers, or both.

Several chemicals have been found to accelerate the plasticization of the emulsion-formed polychloroprene. The most effective compounds are alkalies such as magnesium oxide, ammonium hydroxide, and sodium hydroxide. Weak organic bases, such as the guanidines, are also recommended to aid the breakdown. Material that has been softened by milling under water or with chemical agents can be kept for weeks or months at room temperature without greatly changing in plasticity. . .

No vulcanization agent is necessary, although in commercial practice compounding ingredients are used that seem to act in a similar manner. Metallic oxides, such as magnesium oxide, zinc oxide, and litharge, are usually used for this purpose. Sulfur acts as an accelerator. Organic accelerators have little, if any, effect.
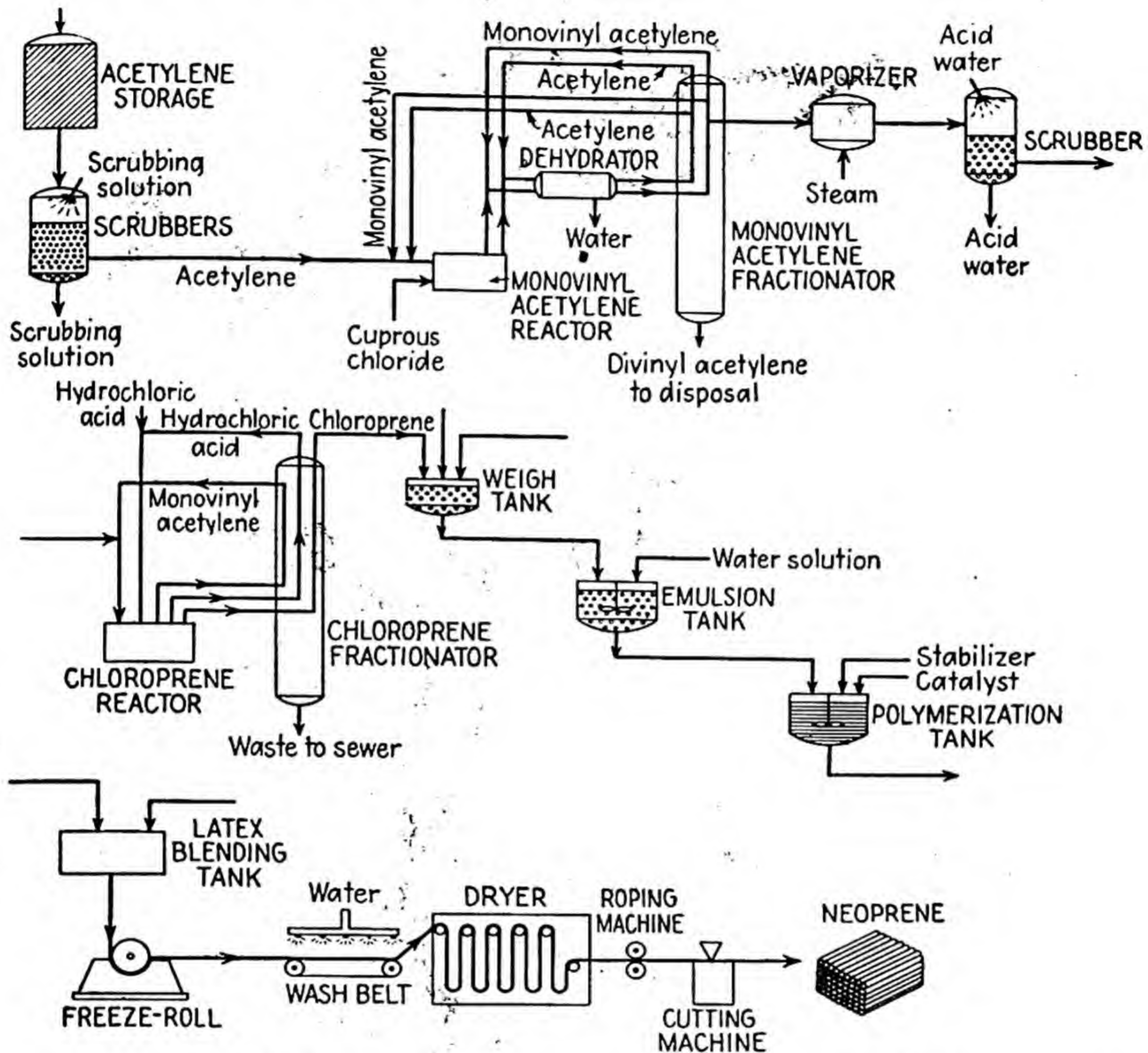
FIG. 108.—Flow sheet for neoprene. (*Chem. and Met.*)

Carbon black has little effect on polychloroprene vulcanizates except to increase their stiffness. The resistance of reinforced vulcanizates to swelling in solvents is far superior to natural rubber and GR-S, but somewhat less than that of the polysulfide and butadiene-acrylonitrile rubbers.

The polychloroprenes are similar to natural rubber in their properties but are greatly superior in resistance to sunlight, atmospheric oxygen and ozone, gas diffusion, heat, flame, oils, solvents, and chemicals. Several types of compounded polychloroprene are available, all of which have the same general properties but differ from each other in specific properties. In general, they have considerably greater densities, slightly lower tensile strength, lower tear resistance, and slightly poorer electrical properties

than natural rubber. Abrasion resistance, particularly at higher temperatures, is better than natural rubber. However, the marked resistance of neoprene to severe conditions such as high temperatures, oils, and chemicals is the principal property that makes it valuable for many applications.

Polychloroprene is also marketed in the form of special lattices for various applications. They may be substituted for natural rubber latex

Fig. 109.—Neoprene sheet being formed into rope to be cut into rods for packaging. (*E. I. du Pont de Nemours & Co.*)

where a vulcanizate possessing oil, heat, sunlight, flame, and age-resistance is desired. Lattices of varying concentrations can be obtained, ranging in general from 50 to 60 per cent solids content.

Polychloroprene was developed not as a rubber substitute but as a synthetic for special uses dependent on its properties. Flexible tubes and hoses for handling petroleum products comprise a large outlet for polychloroprene. Large hose such as that used on tankers is made of poly-

chloroprene. Storage tanks for petroleum products and chemicals are lined with this material. Electrical insulation on flexible wires and cables to be used in contact with oil is a big outlet for neoprene. Molded goods, such as flashlight cases and sockets for electrical connections, shoe soles, and gloves, are made of polychloroprene when resistance to oil is required. An important use of polychloroprene is for printing and industrial rollers where solvents soon cause the breakdown of most resilient materials. In many places, packings and gaskets of polychloroprene which stand up for long periods of service have replaced fibrous materials lacking resilience.

Polychloroprene has been used in industrial truck tires and pneumatic tires for special purposes, but it has not been generally used for tire production. Urgent military requirements during the war period for gasoline-tank linings, cable coverings, gaskets, and a large number of aircraft parts consumed practically all the neoprene that could be produced

Polysulfide Rubbers.—The condensation reactions between organic dihalides and sodium polysulfide produce polymers that conform to the present concept of synthetic rubbers, even though some of them have a sulfur content of over 80 per cent. The generalized reaction for their formation is usually expressed as follows, although two or three atoms of sulfur can be introduced in place of four:

$$ClCH_2-R-CH_2Cl + Na_2S_4 \longrightarrow NaCl + \left[-\!\!-\!\!-CH_2-R-CH_2-S_4-\!\!-\!\!- \right]_n$$
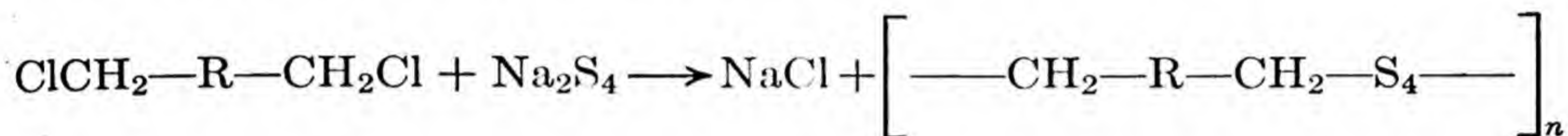
The dihalide may be a normal paraffin with chlorine atoms on the terminal carbons, dichloropropylene hydrin, pentamethylene chloride, or dihalo-ethers like dichlorodiethyl ether and chloropolyethylene oxide. A German synthetic rubber known as Perduren H is formed from dichloroethyl formaldehyde acetal and sodium tetrasulfide. A polysulfide rubber from ethylene diglycoside and sodium tetrasulfide has been used in Japan. Vulcaplas, a polysulfide rubber formed from glycerol dichlorohydrin and sodium tetrasulfide, is marketed in England. Of the paraffinic dihalides, ethylene dichloride, propylene dichloride, and dichlorodiethyl ether are most commonly used in this country

The source raw materials are in abundant supply. The sodium tetrasulfide comes from sodium sulfide and crude sulfur, and ethylene is the chief source of the dihalides. Almost limitless amounts of all three could be made available.

The polymerization reaction is carried out by the emulsion method whereby a solution of sodium polysulfide containing magnesium hydroxide as a dispersing agent is used to emulsify ethylene chloride. The latex that is produced is coagulated by acidification with hydrochloric acid, cut up, washed free of soluble salts, dried, and shredded (see Fig. 110).

There is a considerable difference in the reactivity of the sulfur atoms. Heating with sodium hydroxide removes two sulfur atoms, but more drastic conditions have no effect on the remaining two atoms. Attempts to remove sulfur by solvents or distillation have been unsuccessful, indicating that the sulfur is not merely in solution in the solid.
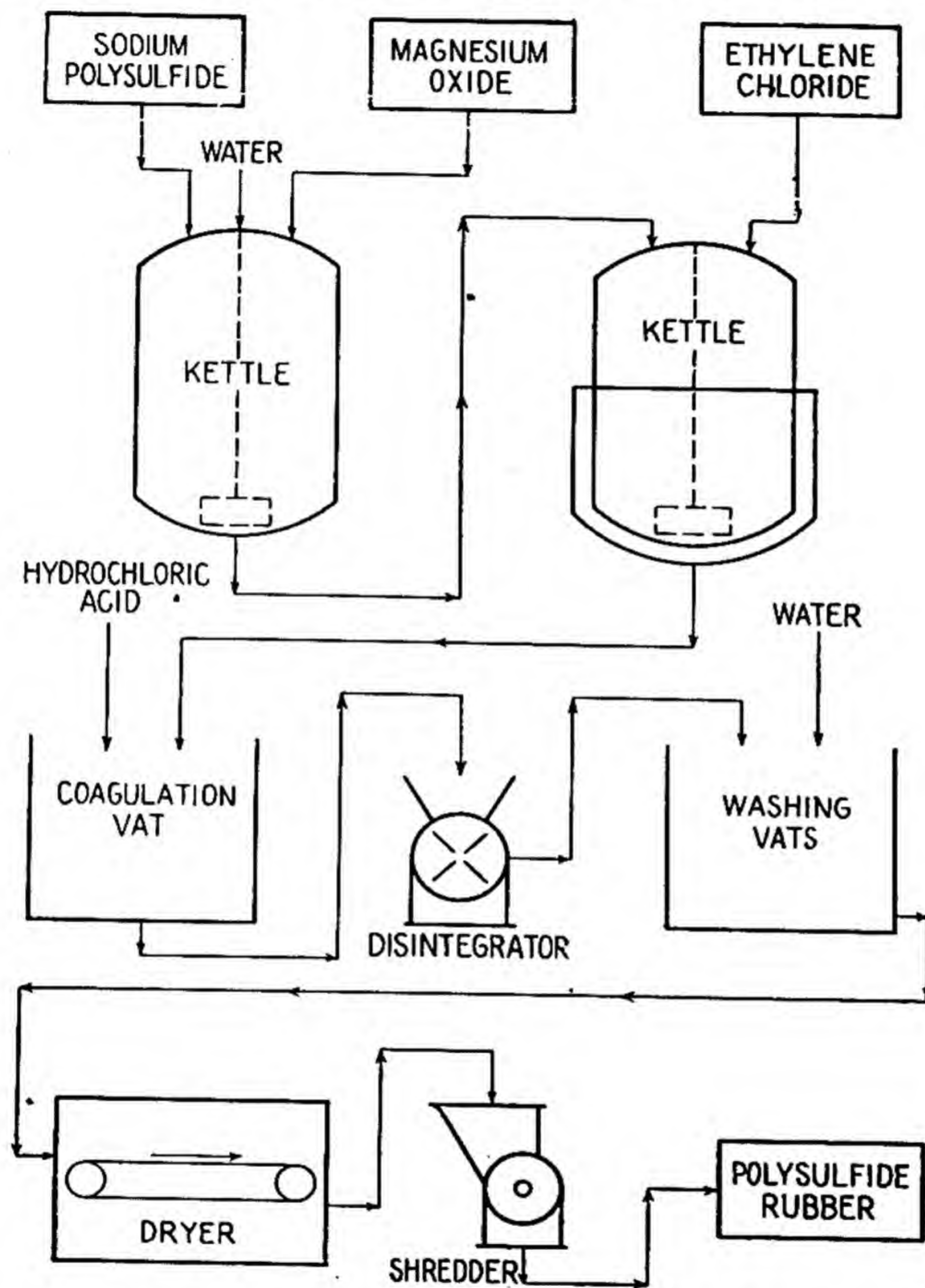
FIG. 110.—Flow sheet for polysulfide rubber.

Various formulas have been advanced to depict the arrangement of the sulfur atoms in the polymer which would explain the difference in reactivity. The most acceptable one that covers the known facts is as follows:

$$-\!\!-\!CH_2CH_2-\!\!\underset{\underset{S}{\overset{S}{\parallel}}}{S}-\!\!\underset{\underset{S}{\overset{S}{\parallel}}}{S}-\!\!CH_2CH_2-\!\!-$$
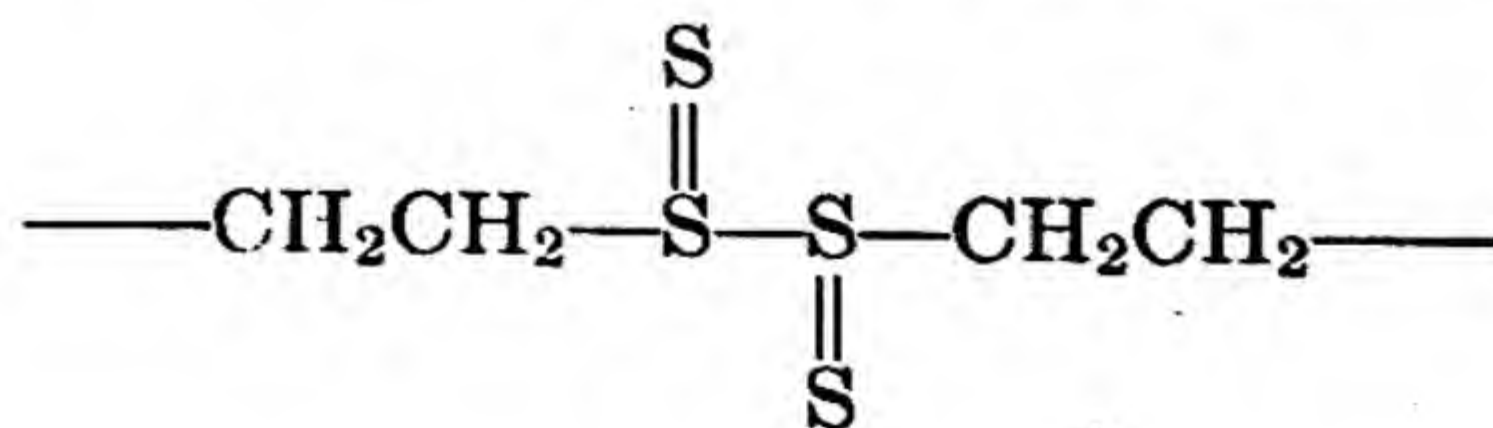
The polysulfide rubbers can be vulcanized, like neoprene, with the metallic oxides as vulcanizing agents and sulfur as an accelerator. The chemical reaction must be of a type somewhat different from that in the vulcanization of natural rubber, where there is a decrease in the number of double bonds in the long-chain molecules; for the polysulfide rubbers an oxidation with the evolution of water and an increase in chain length have been suggested.[1] Fillers are usually required for the development
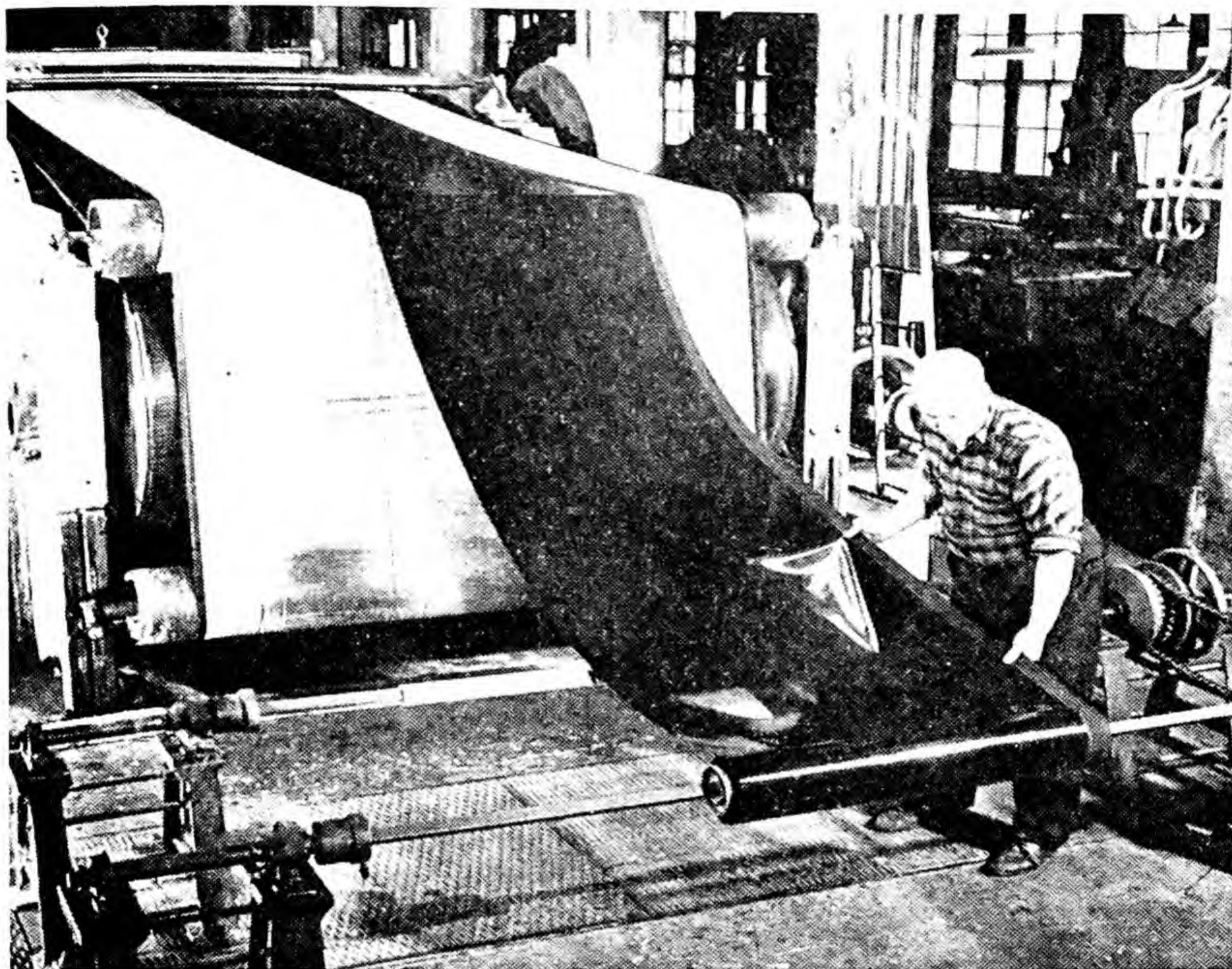
Fig. 111.—Polysulfide sheeting emerging from calender.   (*Thiokol Corp.*)

of satisfactory tensile strength.   Carbon black is most frequently employed for this purpose.

The polysulfide rubbers are by far the most resistant of the synthetic rubbers to the effects of certain liquids such as solvents and oils which are injurious to natural rubber.   Their chief disadvantages are a rather unpleasant odor and some deficiency in mechanical properties.   The odor has, however, been considerably reduced and rendered less objectionable in some of the newer varieties and practically eliminated in others.   Cold flow is a mechanical deficiency that can be reduced somewhat by increase of the amount of filler or by mixture with other types of rubber, natural or synthetic.   Thiokol A is recommended for use only at temperatures

[1] PATRICK, J. C., *Trans. Faraday Soc.*, **32**, 347 (1936).

between −10 and +70°C., but many of the other types are serviceable from about −40 to +80°C.

Stocks can be made to compare with natural rubber in resiliency, and suitable flexible characteristics can be attained. Where oil conditions are encountered, the polysulfide rubbers are markedly superior to natural rubber. Tensile strengths up to 1,400 lb. per sq. in. and elongations of 500 to 600 per cent are obtained with some stocks. Polysulfide rubber is not affected by dilute acids and alkalies, but concentrated sulfuric, nitric, and hydrochloric acids will destroy it.

Practically all the uses of the polysulfide rubbers depend on the excellent solvent resistance of the material. Seals, gaskets, diaphragms, valve-seat disks, flexible mountings, and hose of all types for use in contact with solvents are made of polysulfide rubber. Refined and crude petroleum products are handled through bare hose made from polysulfide rubber. Its use for balloons and special tubing depend on this rubber's low permeability to gases. Boats, life vests, and rafts made of fabric impregnated with this material and inflated with carbon dioxide are also used e tensively. Considerable polysulfide rubber is used in the printing industry for printing-press rollers and blankets (see Fig. 111).

Large underground concrete storage tanks for petroleum products are completely lined with polysulfide. Metal tanks can be successfully coated by the use of the Schori flame process for sprayed-on coatings.

APPENDIX

COMPARATIVE PHYSICAL PROPERTIES OF THE PRINCIPAL PLASTIC MOLDING MATERIALS AND RUBBERS

The chart and table included on the following pages give the relative properties of the principal plastics and rubbers, respectively. Both of these comparisons are general and should not be used for specific information for a particular use, although they do give a ready, quick means of obtaining relative qualities with respect to certain properties. Each characteristic or property varies according to the exact formulation used in preparing the plastic or in compounding the rubber, and the relative qualities may be influenced by special conditions.

The influence of the formulations used in preparing plastics and rubbers frequently has as marked an effect on the resulting properties as does the alloying of metals. In addition, the properties of high polymers are affected by average molecular weight, molecular weight distribution, etc. For these reasons, comparative charts and tables such as the following should be used to obtain only a quick relative comparison of properties. The final choice of a plastic material or a rubber for a particular use requiring specific properties should be made only after consultation with experienced fabricators or after extensive tests that are capable of revealing the suitability of the material for that particular use.

Included in the chart are references to standard tests employed to evaluate the property, principal conditions of the test, and a diagrammatic sketch representing the test procedure. The block in each column indicates the extreme practical range obtainable for standard grades of each material.
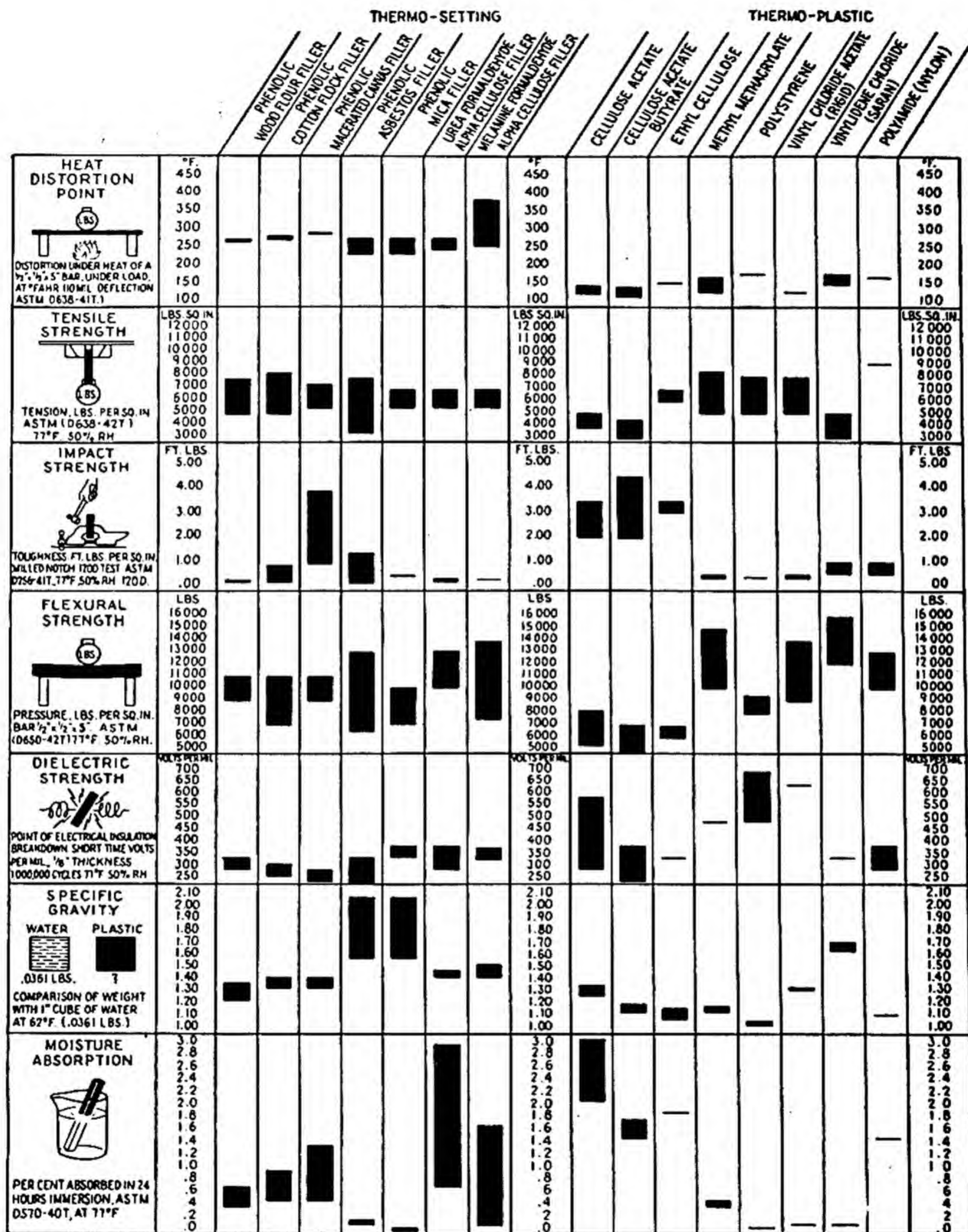
FIG. 112.—Chart illustrating relative properties of common molding materials. (*Chicago Molded Products Co.*)

TABLE 8.—RELATIVE PROPERTIES OF NATURAL AND SYNTHETIC RUBBER*

Property	Natural rubber	Neoprene	Polysulfide	Nitrile rubber	GR-S	Butyl
Workability	Excellent	Good	Fair	Good	Good	Good
Vulcanizing properties	Excellent	Excellent	Fair	Excellent	Excellent	Good
Adhesion to metals	Excellent	Excellent	Poor	Excellent	Excellent	Good
Adhesion to fabrics	Excellent	Excellent	Fair	Good	Good	Good
Resistance to swelling in lubricating oil	Poor	Good	Excellent	Excellent	Poor	Poor
Resistance to deterioration in oil	Poor	Excellent	Fair	Excellent	Poor	Good
Aromatic hydrocarbons	Poor	Poor	Good	Fair	Poor	Fair
Chlorinated hydrocarbons	Poor	Poor	Good	Good	Poor	Poor
Lacquer solvents	Poor	Poor	Good	Fair	Poor	Poor
Gas diffusion	Fair	Good	Excellent	Good	Fair	Excellent
Resistance to diffusion of petroleum products	Poor	Fair	Excellent	Excellent	Poor	Poor
Adaptability for contact with food †	Excellent	Fair	Poor	Fair	Fair	Good
Dielectric strength †	Excellent	Fair	Fair	Fair	Excellent	Fair
Electrical conductivity †	Fair	Fair ‡	Fair	Fair ‡	Fair	Fair
Resistance to water absorption †	Fair	Good	Fair	Good	Good	Good
Strong oxidizing agents	Poor	Poor	Poor	Poor	Poor	Good
Other corrosives	Good	Good	Good	Good	Good	Good
Tensile strength †	Excellent	Good	Fair	Excellent	Good	Excellent
Elongation	Excellent	Excellent	Fair	Excellent	Good	Fair
Resistance to cold flow †	Excellent	Good	Poor	Excellent	Excellent	Excellent
Sunlight †	Fair	Excellent	Excellent	Good	Fair	Excellent
Ozone †	Fair	Excellent	Excellent	Good	Fair	Excellent
Aging	Good	Excellent	Excellent	Excellent	Excellent	Excellent
Approx. specific gravity basic material	0.93	1.23	1.34	1.00	0.94	0.92
Heat resistance †	Good	Excellent	Poor	Excellent	Excellent	Excellent
Flame resistance	Poor	Good	Poor	Poor	Poor	Poor
Cold resistance †	Excellent	Good	Fair	Good	Excellent	Good
Rebound elasticity (snap)	Excellent	Good	Good	Fair	Good	Poor
Abrasion ‡	Excellent	Good	Poor	Excellent	Excellent	Fair
Tear resistance ‡	Excellent	Good	Poor	Good	Fair	Good
Abrasion resistance—soaked in oil	Poor	Fair	Poor	Excellent	Poor	Poor
Color range	Good	Good	Poor	Good	Good	Good
Freedom from odor ‡	Excellent	Fair	Poor	Fair	Good	Good
Resistance to paint and ink driers	Poor	Excellent	Excellent	Excellent	Excellent	Excellent

* Courtesy of B. F. Goodrich Co.
‡ Electrically conductive compounds with more rubbery characteristics can be made of these synthetics than is the case with natural rubber, which has to be heavily loaded to attain the same degree of conductivity

† These properties available only in specific compounds.

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INDEX OF TRADE NAMES AND COMPANIES

Table 9 lists the various companies that supply the plastics industry with resins, plastics, and plastic products. Table 10 lists the various trade names of these products, the type of product, and by means of a numeral keyed with Table 9, the company using the trade name. In general, the companies listed are those supplying the raw materials of the plastics industry, although in some cases finished products are also produced, and does not include a list of the various fabricators. The list of trade names is not complete since it does not include the numerous trade names used by fabricators and jobbers, but it does include the trade names of the principal suppliers of resins and plastic materials.

<div align="center">

TABLE 9.—COMPANIES

</div>

1. Allied Chemical and Dye Corporation
   Barret Division, New York, N. Y.
2. American Bemberg Corporation
   New York, N. Y.
3. American Cellulose Company
   Indianapolis, Ind.
4. American Cyanamid Company
   New York, N. Y.
5. American Enka Corporation
   Enka, N. C.
6. American Hard Rubber Company
   New York, N. Y.
7. American Plastics Corporation
   New York, N. Y.
8. American Viscose Corporation
   Wilmington, Del.
9. Aralac, Inc.
   Bristol, Conn.
10. Atlas Powder Company
    Stamford, Conn.
11. Bakelite Corporation
    Unit of Union Carbide and Carbon Corporation
    New York, N. Y.
12. Bell Telephone Laboratories
    New York, N. Y.
13. Bryant Electric Company
    Hemco Plastics Division
    Bridgeport, Conn.
14. Carbide and Carbon Chemical Company
    New York, N. Y.
15. Casein Company of America
    New York, N. Y.
16. Catalin Corporation
    New York, N. Y.
17. Celanese Corporation of America
    New York, N. Y.
18. Celanese Plastics Corporation
    Division of Celanese Corporation of America
    New York, N. Y.

19. Ciba Products Corporation
    Hoboken, N. J.
20. Colt's Patent Fire Arms Manufacturing Company
    Hartford, Conn.
21. Columbia Chemical Division
    Pittsburgh Plate Glass Company
    Pittsburgh, Pa.
22. Columbian Rope Company
    Auburn, N. Y.
23. Continental-Diamond Fiber Company
    Newark, Del.
24. Cordo Chemical Corporation
    Norwalk, Conn.
25. Delaware Rayon Corporation
    New Castle, Del.
26. Detroit Macoid Corporation
    Detroit, Mich.
27. Detroit Paper Products Corporation
    Detroit, Mich.
29. Dow Chemical Company
    Midland, Mich.
29. Dow-Corning Corporation
    Midland, Mich.
30. E. I. du Pont de Nemours and Company
    Wilmington, Del.
    Arlington, N. J.
    Fairfield, Conn.
31. Durez Plastics and Chemicals, Inc.
    North Tonawanda, N. Y.
32. Durite Plastics, Inc.
    Philadelphia, Pa.
33. Eastman Kodak Company
    Rochester, N. Y.
34. Ellis-Foster Company
    Montclair, N. J.
35. Firestone Industrial Products Company
    Akron, Ohio
36. Firestone Rubber and Latex Product Company
    Fall River, Mass.
37. Firestone Tire and Rubber Company
    Akron, Ohio
    Fall River, Mass.
38. Formica Insulation Company
    Cincinnati, Ohio
39. Freydberg Brothers-Strauss, Inc.
    New York, N. Y.
40. Gemloid Corporation
    Elmhurst, Long Island, N. Y.
41. General Electric Company
    Schenectady, N. Y.
    Pittsfield, Mass.
    Bridgeport, Conn.

42. B. F. Goodrich Company
    Akron, Ohio
    Cleveland, Ohio—Chemical Division
43. Goodyear Tire and Rubber Company, Inc.
    Akron, Ohio
44. Hartford Rayon Corporation
    Rocky Hill, Conn.
45. Haskelite Corporation
    Chicago, Ill.
46. Haskelite Manufacturing Corporation
    Grand Rapids, Mich.
47. Haveg Corporation
    Marshallton, Del.
48. Hercules Powder Company
    Wilmington, Del.
49. Hewitt Rubber Company
    Buffalo, N. Y.
50. Hodgman Rubber Company
    Framingham, Mass.
51. Hood Rubber Company
    Watertown, Mass.
52. Hycar Chemical Company
    Akron, Ohio
53. Industrial Rayon Corporation
    Cleveland, Ohio
54. Industrial Tape Corporation
    New Brunswick, N. J.
55. Irvington Varnish and Insulator Company
    Irvington, N. J.
56. Kimberly-Clark Corporation
    Neenah, Wis.
57. Libby-Owens-Ford Glass Company
    Toledo, Ohio—Plaskon Division
58. Makalot Corporation
    Boston, Mass.
59. Manufacturers Chemical Corporation (Chemaco Corporation)
    Berkeley Heights, N. J.
60. Marathon Corporation
    Chemical Division
    Rothschild, Wis.
61. Marblette Corporation
    Long Island City, N. Y.
62. Marco Chemicals, Inc.
    Sewaren, N. J.
63. Masonite Corporation
    Laurel, Miss.
64. Mica Insulator Company
    New York, N. Y.
65. Monsanto Chemical Company
    St. Louis, Mo.
    Springfield, Mass.—Plastics Division

66. National Dairy Products Corporation
    New York, N. Y.
67. National Rayon Corporation
    Cleveland, Ohio
68. National Vulcanized Fibre Company
    Wilmington, Del.
69. Neville Company
    Pittsburgh, Pa.
70. New Bedford Rayon Corporation
    New Bedford, Mass.
71. Newport Industries, Inc.
    Pensacola, Fla.
72. Nixon Nitration Works
    Nixon, N. J.
73. North American Rayon Corporation
    Elizabethton, Tenn.
74. Pennsylvania Coal Products Company
    Petrolia, Pa.
75. Pittsburgh Plate Glass Company
    Columbia Chemical Division
    Pittsburgh, Pa.
76. Plax Corporation
    Hartford, Conn.
77. Reichhold Chemicals, Inc.
    Detroit, Mich.
78. Reilly Tar and Chemical Corporation
    New York, N. Y.
79. Resinous Products and Chemical Company
    Philadelphia, Pa.
80. Richardson Company
    Lockland, Ohio
81. Röhm and Haas Company
    Philadelphia, Pa.
82. St. Regis Paper Company
    Panelyte Division
    New York, N. Y.
83. Shawinigan Products Corporation
    New York, N. Y.
84. Sherwin-Williams Company
    Cleveland, Ohio
85. Skenandoa Rayon Corporation
    Utica, N. Y.
86. Standard Chemical Company
    Akron, Ohio
87. Standard Oil Company of New Jersey
    New York, N. Y.
88. Sylvania Industrial Corporation
    New York, N. Y.
89. Synthane Corporation
    Oaks, Pa.
90. Synthetic Latex Corporation
    New York, N. Y.

91. Tennessee Eastman Corporation
    Kingsport, Tenn.
92. Thiokol Corporation
    Trenton, N. J.
93. Tubize-Chatillon Corporation
    New York, N. Y.
94. Union Bay State Company
    Cambridge, Mass.
95. U. S. Industrial Alcohol Company
    Newark, N. J.
96. U. S. Industrial Chemicals, Inc.
    New York, N. Y.
97. United States Plywood Corporation
    New York, N. Y.
98. U. S. Rubber Company
    New York, N. Y.
    Akron, Ohio
99. U. S. Stoneware Company
    Akron, Ohio
100. Watertown Manufacturing Company
    Watertown, Conn.
101. Westinghouse Electric and Manufacturing Company
    East Pittsburgh, Pa.

TABLE 10

Trade name	Type of product	Company
Abalyn	Methyl abietate resins	48
Acele	Cellulose acetate rayon	30
Aceloid	Cellulose acetate plastics	3
Acclose	Cellulose acetate	3
Acryloid	Acrylic resin solutions	81
Acrysol	Acrylic resin emulsions	81
Agripol	Vulcanizable vegetable-oil polymers	77
Akeo	Phenolic varnish and lacquer resins	4
Allite	Cast allyl resin	75
Allymer	Allyl monomers	75
Alvar	Vinyl resins	83
Amberlac	Alkyd varnish and lacquer resins	79
Amberlite	Phenol-formaldehyde adhesives	79
Amberol	Phenolic varnish and lacquer resins	79
Amer-glo	Cellulose nitrate plastics	18
Ameripol	Butadiene-acrylonitrile copolymer	42
Amerith	Pyroxylin	18
Ameroid	Casein resins	7
Aqualite	Phenolic-bearing material	68
Aquaplex	Alkyd-emulsion varnish and lacquer resins	79
Aralac	Casein fibers	9, 66
Aristocrat	Cuprammonium rayon	2
Arochem	Oil-modified alkyds	96

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Aroclor	Chlorinated diphenyl varnish and lacquer resins	65
Arodure	Urea-formaldehyde resins	96
Arofene	Oil-soluble phenolic resins	96
Aroplaz	Oil-modified alkyds	96
Avisco	Viscose rayon (staple fiber)	8
Avtex	Phenolic moldings and sheet stock	51
Bakelite	Phenolic resins	11
Beckacite	Phenol and maleic resins	77
Beckamine	Urea-formaldehyde coating resins	77
Beckopol	Phenolic varnish and lacquer resins	77
Beckosol	Alkyd resins	77
Beetle	Urea-formaldehyde molding materials	4
Beetleware	Urea-formaldehyde plastics	4
Bemberg	Cuprammonium rayon	2
Benalite	Lignin plastics	63
Benaloid	Lignin plastics	63
Briglo	Viscose rayon	5
Butacite	Polyvinyl butyral resins	30
Butaprene	Butadiene copolymers	37
Butyl rubber	Isobutene-diolefin copolymer	87
Buvar	Polyvinyl butylral resins	83
Cascamite	Urea-formaldehyde adhesive	15
Cascophen	Phenol-formaldehyde adhesive	15
Casco resin	Urea-formaldehyde adhesive	15
Catabond	Phenolic laminating resin	16
Catalin	Cast phenol-formaldehyde resins	16
Catalin melamine	Melamine resins	16
Catapak	Lignin molding compound	16
Catavar	Phenolic coating resins	16
Celairese	Acetate rayon (staple fiber)	17
Cellanite	Phenolic laminated products	23
Cellucraft	Cellulose nitrate coating	26
Cellulak	Shellac-paper laminated tubing	23
Celluloid	Cellulose nitrate plastics	18
Celoron	Molded phenolic plastics	23
Cerex	Modified polystyrene	65
Chacelon	Acetate rayon	93
Chalkcelle	Viscose rayon	8
Chardonize	Viscose rayon	93
Chemigum	Butadiene-acrylonitrile copolymers	43
Cibanite	Aniline-formaldehyde resin	19
Coltrock	Phenol-formaldehyde plastics	20
Coltwood	Phenol-formaldehyde plastics	20
Compregnite	Liquid phenol-formaldehyde impregnating solution	15
Cordo-Bond	Adhesives	24

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Cordura	Viscose rayon (high tenacity)	30
Co-Ro-Lite	Resin-impregnated fiber fillers and moldings	22
Crown	Viscose rayon	8
CR resins	Allyl resins	21
Crystle	Clear phenolic resins	61
Cumar	Paracoumarone-indene resins	1
Delray	Viscose rayon	25
Dilectene	Aniline formaldehyde resins	23
Dilecto	Phenol-formaldehyde laminated products	23
Dow-Corning fluids	Liquid silicones	29
Dulesco	Viscose rayon	8
Dul-Tone	Viscose rayon	53
Dulux	Alkyd varnish resins	30
Du Pont modified polyvinyl butyral	Vinyl acetal resins	30
Du Pont rayon	Viscose rayon	30
Duraloy	Phenol-formaldehyde laminated products	27
Duramold	Laminated plywood	45
Duraplex	Alkyd varnish resins	79
Durez	Phenol-formaldehyde resins	31
Durite	Phenol-formaldehyde and phenol-furfural molding compounds and resins	32
Durophane	Transparent plastic wrapping film	37
Dyal	Alkyd resin solutions	84
Eastman	Acetate rayon	91
Elfolite	Maleic thermosetting resin	24
Englo	Viscose rayon	5
Ethocel	Ethyl cellulose	28
Ethomelt	Ethyl cellulose for coating	28
Ethomulsion	Ethyl cellulose for sizing	28
Etho-Raon	Ethyl cellulose fibers and yarn	28
Fairprene	Chloroprene polymer for fabric coating	30
Fiberlac	Cellulose nitrate lacquer	65
Fibestos	Cellulose acetate	65
Fibro	Viscose rayon (staple fiber)	8
Flamenol	Polyvinyl chloride	41
Flotofom	Plastic foam	98
Foamex	Foamed plastic	36
Formex	Polyvinyl acetal wire coating	41
Formica	Laminated phenolics	38
Formvar	Polyvinyl formal	83
Fortisan	Acetate rayon	17
Gelva	Vinyl resins	83
Gemloid	Acrylics and cellulose acetate	40
Geon	Polyvinyl chloride resins	42
Geon latex	Water dispersion of polyvinyl chloride	42
Glyptal	Alkyd varnish and lacquer resins	41

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Hartford	Viscose rayon	44
Haskelite	Plywood bonded with phenolic resin	46
Haveg	Asbestos-filled phenolic products	47
Hercolyn	Hydrogenated methyl abietate	48
Hercose	Cellulose acetate-butyrate	48
Hercose AP	Cellulose acetate-propionate	48
Herculoid	Cellulose nitrate	48
Heroprene	Neoprene	49
High Narco	Viscose rayon (high tenacity)	73
Horco X	Thermosetting polyvinyl butyral	50
Hycar OR-15, OR-25, OS-10	Butadiene-acrylonitrile copolymers	52
Hy-Flex	Extruded plastic tubing	55
Hygram	Viscose rayon (high tenacity)	93
Indur	Phenolic molding compounds	78
Insurok	Phenol-formaldehyde molded and laminated plastics	80
Irv-O-Lite	Extruded vinylites	55
Ivaleur	Cellulose nitrate plastics	18
Kacelite	Resin-impregnated papers for laminating	56
Kaurite	Urea-formaldehyde resins	57
Kavtex	Polyvinyl chloride	43
K.E.M.	Thermosetting molding compound	58
Kem-pol	Vulcanizable vegetale-oil polymers	84
Keratol	Cellulose nitrate coated fabrics	10
Kimpreg	Resin-impregated papers	56
Koda	Acetate rayon	91
Kodafilm	Cellulose nitrate	33
Kodaloid	Cellulose nitrate	33
Kodapak	Cellulose acetate foil	33
Korogel	Polyvinyl chloride gel	42
Korolac	Polyvinyl chloride coating composition	42
Koroseal	Polyvinyl chloride resins	42
Krene	Vinyl chloride-acetate copolymer	14
Kriston	Allyl resin	42
Kurilac	Shellac	30
Lamicoid	Laminated sheets, rods, tubes	64
Laminac	Polyester resins	4
Lignolite	Laminated lignin plastic	60
Loabond	Styrene laminating resin	16
Loalin	Styrene molding powders	16
Loavar	Styrene coatings	16
Lucite	Polymethyl methacrylate resins	30
Lumapane	Wire-reinforced plastic glazing material	18
Lumarith	Cellulose acetate	18
Lumarith E. C.	Ethyl cellulose	18
Lumarith V. N.	Polyvinyl base foil	18
Lustron	Polystyrene	65

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Macite	Cellulose acetate	59
Macoid	Cellulose nitrate dip coating	26
Makalot	Phenol-formaldehyde resins	58
Marblette	Phenol-formaldehyde cast and liquid resins	61
Marcolite	Polyester laminates	62
Matesa	Cuprammonium rayon	2
Melantine	Melamine-formaldehyde resins	19
Melmac	Melamine-formaldehyde resins	4
Melocol	Polyamide-formaldehyde resins	19
Melopas	Polyamide-formaldehyde resins	19
Melurac	Melamine-urea-formaldehyde adhesives	4
Methocel	Methyl cellulose	28
Micarta	Laminated, molded-laminated, molded-macerated plastics	101
Mir-Con	Laminated phenolic, paper base	27
National	Viscose rayon	67
Neillite	Phenolic molding resins	100
Neoprene	Polychloroprene	30
Nevidene	Coumarone resins	69
Nevillac	Coumarone-indene resins	69
Neville	Coumarone-indene resins	69
Nevindene	Coumarone-indene resins	69
Nevtex	Coumarone-indene coating resins	69
Newbrary	Viscose rayon	70
Newdull	Viscose rayon	70
Newlow	Viscose rayon	70
Nitron	Cellulose nitrate sheets, rods, and tubes	65
Nixon ethyl cellulose	Ethyl cellulose	72
Nixonite	Cellulose acetate	72
Nixonoid	Cellulose nitrate plastics	72
North American	Viscose rayon	73
Nuba	Resinous coal-tar pitch	69
Nubun	Butadiene copolymer	98
Nuro	Polymerized rosin	71
Nylon	Polyamides	30
Nylon FM-1	Polyamide molding powder	30
Nypene	Polyterpene resin	69
Okon	Cold-molded bituminous resins	6
Panelyte	Phenol-formaldehyde plastics	82
Paracon	Vulcanized polyester	12
Paradene	Coumarone-indene resins	69
Parafilm	Rubber composition	60
Paraplex	Varnish and lacquer resins	79
Paraplex X-100	Polyester elastomer	79
Parlon	Chlorinated rubber	48
Pascophen LT-67	Phenolic adhesive	15
P.A.W	Neoprene sealing tape	30

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Penscolite	Resorcinol-formaldehyde resins	74
Pentalyn-G	Pentaerythritol resin	48
Perbunan	Butadiene-acrylonitrile copolymer	87
Perglo	Viscose rayon	5
Petrex	Terpene-maleic anhydride resin	48
Pexide 851	Polymerized rosin	48
Phemaloid	Resin-bonded plywood	46
Phenac	Phenolic varnish resins	4
Phenester	Modified coumarone-indene resins	69
Plaskon	Urea-formaldehyde resins	57
Plaskon melamine	Melamine resin	57
Plastacele	Cellulose acetate	30
Plax methacrylate	Polymethyl methacrylate	76
Plexiglas	Polymethyl methacrylate	81
Plexon	Resin-coated fibers	39
Pliofilm	Rubber hydrochloride	43
Plioflex	Polyvinyl chloride	43
Plioform	Modified isomerized rubber	43
Plyamine	Urea-formaldehyde for bonding	77
Plymetl	Resin-bonded plywood	46
Plymold	Resin-bonded plywood	46
Plyophen	Phenol-formaldehyde resins	77
Polyfibre	Fibrous polystyrene	28
Polyflex	Flexible polystyrene sheet	76
Polym	Phenolic resin varnish	34
Pregwood	Phenolic impregnated plywood	38
Premier	Viscose rayon	53
Prenite	Neoprene F	42
Primal	Acrylic resin for leather finishes	81
Prystal	Cast phenol-formaldehyde	16
PVA	Polyvinyl alcohol	30
Pyralin	Cellulose nitrate plastic	30
Rauxite	Urea-formaldehyde varnish resins	95
Rauxone	Alkyd varnish resins	95
Rauzene	Phenolic varnish and lacquer resins	95
Reanite	Plastic adhesive	99
Resimene	Melamine resins	65
Resinox	Phenol-formaldehyde resins	65
Rezyl	Alkyd varnish resins	4
Rhonite	Urea-formaldehyde resin	81
Rhoplex	Acrylic resin for textile finishes	81
Ruba	Synthetic rubber	90
Rubide	Rubber chloride	37
Rubprene	Neoprene	37
Saflex	Polyvinyl butyral	65
Saran	Vinylidene–vinyl chloride copolymers	28
S.D.O.	Synthetic drying oil	30

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Seraceta	Acetate rayon	8
Seraceta Fibro	Acetate rayon (high tenacity)	8
Skenandoa	Viscose rayon	85
Snowkrepe	Cuprammonium rayon	2
Solvar	Polyvinyl acetate resins	83
Spun-Black	Viscose rayon	53
Spun Lo	Viscose rayon	53
Star Breeze	Cuprammonium rayon	2
Staybelite	Hydrogenated rosin varnish resins	48
Stripcoat	Ethyl cellulose	28
Styraloy	Polystyrene	28
Styramic	Polystyrene	65
Styramic HT	Polydichlorostyrene	65
Styrex	Polystyrene	28
Styrite	Polystyrene	28
Styron	Polystyrene	28
Sundora	Cellulose acetate	30
Supernarco	Viscose rayon (high tenacity)	73
Sylphloc	Viscose tubing	88
Sylphrap	Viscose foil	88
Sylphseal	Viscose	88
Synthane	Phenol-formaldehyde laminated products	89
Tec	Cellulose acetate varnish resins	91
Teca	Acetate rayon	91
Teflon	Polymer of tetrafluoroethylene	30
Teglac	Alkyd varnish and lacquer resins	4
Tego	Phenolic resin for plywood	79
Tekwood	Paper-faced plywood	97
Templus	Phenolic molding compound	13
Tempra	Viscose rayon (high tenacity)	5
Tenasco	Viscose rayon (high tenacity)	8
Tenite I	Cellulose acetate	91
Tenite II	Cellulose acetate-butyrate	91
Texcel	Cellophane tape	54
Textolite	Phenol-formaldehyde laminates	41
Thalid	Allyl polyester	65
Thiokol	Organic polysulfides	92
Transflex	Transparent vinyl tubing	55
Tubize	Viscose rayon	93
Tygon F	Furane resin	99
Tygon T	Modified polyvinyl chloride	99
Tygonite	Plastic bonding cement	99
Tyron	Viscose rayon (high tenacity)	53
Ubagrip	Neoprene adhesive	94
Ubapol	Adhesive	94
Ubatex	Polystyrene emulsion	94
Ubatol	Polystyrene emulsion	94

TABLE 10 (*Continued*)

Trade name	Type of product	Company
Uformite	Urea-formaldehyde resins	79
Urac	Urea-formaldehyde adhesives	4
Uskol	Synthetic rubber	98
Uskon	Conductive coatings	98
Velofilm	Polyvinylidene chloride	37
Veloflex	Polyvinylidene chloride	37
Velon	Polyvinylidene chloride fabrics and film	36
Versiflex	Flexible vinylites	14
V-Film	Polyvinyl chloride foil	43
Vimlite	Cellulose acetate	17
Vinsol	Modified rosin varnish and lacquer resins	48
Vinylite	Vinyl chloride–acetate copolymers	14
Vinylseal	Vinyl acetate adhesives	11
Vinyon	Polyvinyl chloride–acetate fiber	8
Vistanex	Isobutene polymer	87
Vitala	Viscose rayon (high tenacity)	5
Vue-lite	Translucent cellulose acetate	65
Vuepak	Transparent cellulose acetate	65
Vulcoid	Phenolic resin-impregnated vulcanized fiber	23
Weldtex	Plywood	97
Weldwood	Urea-formaldehyde adhesives	97
Xtra-Dull	Viscose rayon	73
Zaflex	Pyroxylin-coated papers	10
Zakaf	Pyroxylin-coated fabric	10
Zapon	Pyroxylin-coated fabrics	10

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LIST OF VISUAL AIDS

The following list of visual aids can be used to supplement some of the material in this book. This list is comprehensive rather than selective. It is, therefore, suggested that each film be previewed before using as some may contain information that is too elementary.

These films can be obtained from the producer or distributor listed with each title. (The addresses of producers and distributors are given at the end of the bibliography.) In many cases these films can be obtained from your local film library or local film distributor; also, many universities have large film libraries from which they can be borrowed.

The running time (min) and whether it is silent (si) or sound (sd) are listed with each title. All those not listed as color (C) are black and white. All of the motion pictures are 16mm

Each of the U. S. Office of Education films has a coordinated silent film-strip and an instructor's manual. In many cases, other films also have accompanying instructor's manuals.

Origin and Synthesis of Plastics Materials (USOE 16min sd). Shows the organic origin of plastics and the resemblance of synthetic compounds to natural substances; synthesis of plastics from natural substances; differences between thermosetting and thermoplastic materials; compounding plastics to provide desired properties in products; forms in which plastics are produced; and typical plastics products.

Methods of Processing Plastics Materials (USOE 21min sd). Presents the fundamentals of the compression, transfer, extrusion, and injection molding methods; the finishing of molded parts; fundamentals of lamination; and machining laminated and other plastics products.

Preparing the Charge and Loading the Mold (USOE 11min sd). Shows how to set up the press; how to weigh the charge; how to preheat the charge; how to clean and lubricate the mold; how to load the mold.

Molding a Simple Part (USOE 10min sd). Shows how to close the mold; how to breathe the mold; how and when to open the mold; how to prevent pieces from warping; and how to coordinate steps of molding cycle.

Molding a Part with Inserts (USOE 10min sd). Shows how transfer molding differs from compression molding; how to determine whether a part should be molded by the transfer method; how to mold a part by the transfer method; how to coordinate the steps of the molding cycles.

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Semiautomatic and Hand Molding of Intricate Parts (USOE 16min sd). Explains how to mold a part with undercuts; how to position the wedges and to close the mold; how to mold a part with complicated shape; how to assemble a hand mold; and how to disassemble a hand mold.

Setting Up the Press and Molding a Part (USOE 16min sd). Shows what happens in the plunger cylinder, heating cylinder, and mold during injection molding; how to set up an injection molding press for a specified job; how to avoid dampness and contamination of molding material; how to maintain the operating cycle and prevent damage to the mold and press.

Machining Laminated Plastics (USOE 19min sd). Shows how to machine typical laminated part; how to cut the tube stock to length on a circular saw; how to turn the outside diameters on a lathe; how to machine inside diameters by boring with a lathe; how to finish the machining of the part on a milling machine.

Production Design and Molding Techniques for Thermosetting Plastics (Princeton 40min sd). Presents solution of some problems of confronting plastics industry.

Selecting the Right Thermosetting Molding Material (Princeton 30min sd). Technical and practical application of thermosetting molding plastics.

Shape of Things to Come (Boonton 33min sd C). A trip through company's plastic material factory showing operation of presses, compression transfer, and injection; illustrates mold construction; use of machine tools and finishing operations; covers new method of heat-molding compounds by radio-frequency currents.

Plastics (YA 16min sd). Tells the story of plastics.

This Plastic Age (Modern Plastics 30min sd C). Shows how plastic resin in the raw may produce lamps, heat-resistant electrical appliances, toys, equipment, etc.

The Magic of Modern Plastics (Breskin 35min sd C). Relates the story of invention of cellulose nitrate to present development; manufacturing stages.

Story of Nitrocellulose (Hercules 45min si). The manufacture and uses of nitrocellulose.

Careers for Cellulose (Hercules 30min sd C). Describes the forming of cotton linters into cellulose derivatives; from the chemical bases are made cellulose plastics, lacquers, film, rayon.

The Fourth Kingdom (Association 20min sd). Development of Bakelite materials and expansion of uses for these man-made products.

Plexiglas (Rohm & Haas 20min sd). Shows inspection and fabrication.

Care and Cleaning of Plexiglas (Rohm & Haas 20min sd). Presents inspection, storage, and use of masking paper; cutting, repairing, cementing ribs, cleaning and buffing to eliminate scratches.

Tygon (US Stoneware 14min si). Manufacture and use of plastic materials.

Story of Formica (Formica 46min sd C). Uses made of laminated plastics and their role in the future.

New World through Chemistry (Du Pont 20min sd C). Shows nylon textile fiber; enoprene synthetic rubber, cellulose sponges; Zelan finish; synthetic dyestuffs and lucite plastic.

Rayon (Minn 31min sd). Manufacture of viscose and acetate rayon.

Rayon, A New Frontier of Progress)Viscose 20min sd). Raw materials and steps involved in manufacture of spun rayon yarn, acetate yarn, mignon yarn; uses of the different kinds of rayon yarn.

Fashion's Favorite (Du Pont Rayon 33min sd MP). Explains the important fundamentals of rayon; shows the entire process of rayon manufacturing from the time the cellulose is received at the rayon plant until the finished yarn is ready for shipment.

Proving Ground (Celanese 25min sd). A Celanese plastic, Lumarith transparent packaging material—its use in packaging.

The Story of Neoprene (DuPont 20min sd). Shows the story of neoprene and the use of this product to replace natural rubber.

Story of Synthetic Rubber (BM 28min sd). Shows the processes in the manufacture of synthetic rubber.

Synthetic Rubber (Goodyear 21min sd). Covers the history of the development of synthetic rubbers; shows step-by-step processes in the making of chemicals into rubber.

SOURCES OF FILMS LISTED ABOVE

Association Fi'ms, Y.M.C.A. Motion Picture Bureau, 347 Madison Ave., New York 17.

BM—U. S. Bureau of Mines Experiment Station, 4800 Forbes St., Pittsburgh 13, Pa.

Boonton Molding Co., Film Office, 122 E. 42nd St., New York 17.

Breskin Publishing Co., Film Booking Office, 122 E. 42nd St., New York 17.

Castle Films, Inc., 30 Rockefeller Plaza, New York 20.

Celanese Plastics Corp., 180 Madison Ave., New York 16.

Du Pont—E. I. Du Pont de Nemours & Co., Inc., Wilmington 98, Del.

Du Pont Rayon—E. I. Du Pont de Nemours & Co., Inc., Rayon Division, Wilmington 98, Del.

The Formica Insulation Co., 4614 Spring Grove, Cincinnati 32, Ohio.

Goodyear Tire & Rubber Co., Inc., 1144 E. Market St., Akron, Ohio.

Hercules Powder Co., Inc., 908 Market St., Wilmington 99, Del.

Minn—University of Minnesota, Bureau of Visual Instruction, Minneapolis 14, Minn.

Modern Plastics Magazine, 122 E. 42nd St., New York 17.
Princeton Film Center, 55 Mountain Ave., Princeton, N. J.
Rohm & Haas Co., Washington Square, Philadelphia 5, Pa.
USOE—U. S. Office of Education (obtainable from Castle Films, Inc.).
U. S. Stoneware Co., 411 E. Market St., Akron, Ohio.
Viscose Co., 140 N. Dearborn, Chicago 2.
YA—Young America Films, Inc., 18 W. 41st St., New York 17.

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